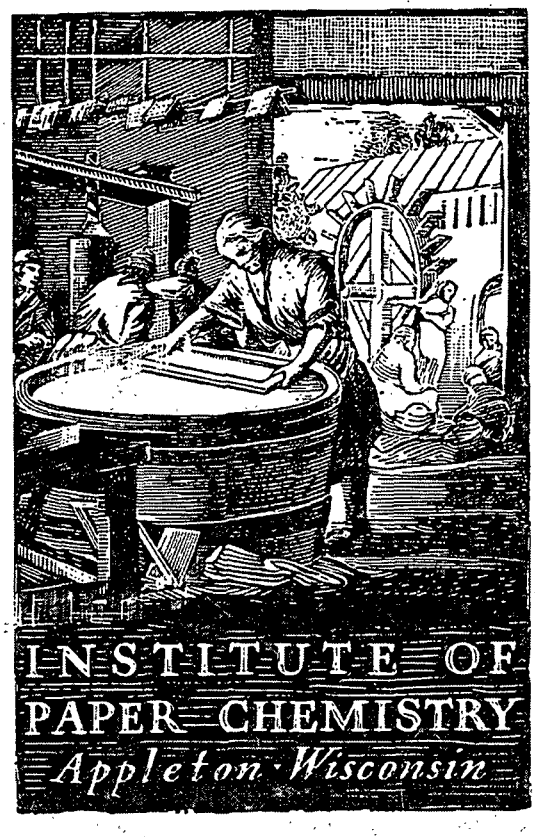

SOLUBILITY LIMITS IN BLACK LIQUOR

Project 3136

Report One

A Progress Report

to

MEMBERS OF GROUP PROJECT 3136

February 22, 1974

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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Appleton, Wisconsin

SOLUBILITY LIMITS IN BLACK LIQUOR

SUMMARY

A study of solubility limits for various compounds in black liquor has been carried out. This study was based on measurement of saturation concentrations under equilibrium conditions. It was established that sodium carbonate and sodium sulfate are the major components which precipitate on concentrating black liquors to 65% solids. These outweigh the organic which precipitates by a substantial margin. Large amounts of organic precipitation were only brought about by acidification of the liquors.

A general correlation for Na_2CO_3 and Na_2SO_4 solubilities in alkaline process black liquors was developed. It is believed to be accurate within 5-10%. It is based on the application of the data of Green and Frattali for the Na_2CO_3-Na_2SO_4-NaOH-H_2O system to black liquor (assuming all of the sodium in the black liquor other than that present as Na_2CO_3 and Na_2SO_4 acts equivalent to NaOH) and a correction factor to account for the increased solubility in high-solids content liquors. This correlation can be used to predict the onset and extent of carbonate-sulfate precipitation for any alkaline process black liquor. The major liquor composition variable affecting solubility is the total sodium content. Liquor solids content is the second most important variable.

Temperature did not have an appreciable effect on the solubility limits over the range 100-120°C. Solubilities of Na_2CO_3 + Na_2SO_4 decrease about 10% from 120 to 140°C. Two other sodium salts, chloride and thiosulfate, were found to be quite soluble in black liquor up to at least 10% on the solids. Their sodium content does influence the solubility of Na_2CO_3 and Na_2SO_4.

An attempt to determine solubility limits for $CaCO_3$ in black liquor was not very successful. It was found that the calcium solubility in black liquor was about one order of magnitude higher than expected based on the solubility of $CaCO_3$ in water.

As a general rule there was little evidence for organic precipitation in these experiments. Most of the organic which did precipitate could be correlated with the soap content of the liquors. Evidence for precipitation of lignin by concentration of black liquors is considered marginal at best. Acidification of liquor did lead to significant lignin precipitation. This was reversible upon addition of NaOH to restore the original pH. Since acidification would not normally be part of a liquor concentration sequence, it was concluded that (so long as the soap content of the liquor is kept low) precipitation of organics should not be a major factor in evaporator scaling. This would be valid if the scales form by precipitation from supersaturated solutions. It is believed that much of the organic content of scale deposits can be attributed to fibers and liquor incorporated into a growing inorganic scale matrix. It is also possible that organic deposits may form by a nonequilibrium process having nothing to do with saturation-type phenomena.

INTRODUCTION

BACKGROUND

Information on the solubility of the various components in black liquor is basic to an understanding of scaling problems during evaporation of black liquor. Solubility limits would define the maximum liquor concentrations obtainable without the potential for scale formation. They also provide a base line for interpreting the effects of operational variables on evaporator scaling.

It is expected that indirect evaporation of black liquors and, hence, scaling problems, will receive increasing attention in the next few years. This will be due to two causes; the more effective utilization of energy which is potentially available in indirect evaporation, and the elimination of the direct contact evaporator as an odor source. Under these conditions, knowledge of solubility limits will be of major value in avoiding or minimizing operating problems. The addition of extraneous chemical streams (such as bleach effluent) to the recovery system could increase the amounts of inorganic chemicals (such as sodium chloride) and this could affect scaling tendencies. Changes in pulping practice could likewise affect the liquor composition and its scaling behavior.

Scaling problems can be especially important in concentrators for achieving very high solids levels. In many cases, the solubility limits of a given liquor, rather than viscosity, govern the final concentration which can be obtained. Arhippainen and Jungerstam (1) state that "Any discussion of operating experience of black liquor evaporation to high dissolved solids must be based on a discussion of the black liquor properties. Our present methods to characterize black liquors can be improved upon, and such improvements seem imperative if some of the operating and design problems in this area are ever to

be mastered." They also state that the influence of the scaling properties is of at least equal importance to high-solids evaporator design as viscosity and boiling point rise. Lankenau and Flores (2) cite three areas where more complete information needs to be developed: upper temperature limitations as a function of solids concentration (set by solubility of liquor components), corrosion problems, and fouling rates and wash cycles for various combinations of liquor characteristics and concentrations.

At the time that this project was initiated, there was some qualitative information available concerning the solubility of black liquor components, but very little quantitative data. Most of the existing information concerned the nature of the material found in evaporator deposits. Berry (3) discussed scaling in black liquor multiple-effect evaporators. He listed sodium sulfate scale, calcium carbonate scale, silicate scale, soap scale, char scale and combinations of fiber with the scale. The silicate scale consists of various sodium-aluminum silicates. The replacement of alumina refractories by chrome ore refractories in the recovery furnace has tended to minimize the formation of the glassy, silicate scales. Backtemann and Marr (4) mention deposits caused by soap, inorganic salts such as Na_2CO_3 and Na_2SO_4, and lignin precipitation. Letonmyaki, et al. (5) examined the change in composition of black liquors during evaporation and the composition of the deposits formed. They found that the content of organic substances in the deposits (38%) was considerably lower than in the black liquors (68%). Despite this lower organic content of the deposits, there was some tendency for resinous substances to accumulate in the deposits. The deposits were considerably enriched in Na_2SO_4. Diedrichs and Hedstrom (6) considered salt incrustations in black liquor evaporators and especially the inorganic salts Na_2SO_4 and Na_2CO_3. They made use of the data of Green and

Fratalli (7) on the inorganic system Na_2SO_4-Na_2CO_3-NaOH-H_2O in estimating equilibrium solubilities in black liquor. Diedrichs and Hedstrom assumed that the organic and other anions which occurred in black liquor had the same effect on the equilibrium solubility of Na_2SO_4 and Na_2CO_3 as the equivalent amount of hydroxyl ion. They estimated the critical dissolved solids content for salt precipitation to be 52% at 3.4% Na_2SO_4 based on solids and 57% dissolved solids content at 1.7% Na_2SO_4 on the solids.

Although there is some data available on the solubility of inorganic salts, particularly solubilities in aqueous solutions, there is very little information on the solubility of the organic substances in black liquors. The nature of the organic substances in black liquor is very complex. Most of the lignin in the black liquor is present as large colloidal macromolecules containing 2-10 phenylpropane units which can undergo slow condensation reactions. Most of the carbohydrate material in the black liquor originates from hemicelluloses, and is present as the sodium salts of various saccharinic acids. There are also extractives, mainly the sodium salts of resin acids and fatty acids (soaps). According to Passinen (8), two colloidal systems exist in black liquor: the macromolecular colloid formed by the alkali lignin, and the association colloids formed by the fatty acid and resin acid salts. Precipitation of organic substances from black liquor is predominantly associated with the stability of these colloids.

The stability of colloidal alkali lignin is attributed to ionized hydrophilic groups which impart an electrical charge to the colloidal particles; moreover, the stability is influenced by a protecting shell of water molecules (8). The most important ionizable hydrophilic groups in the alkali lignin are phenolic hydroxyl groups and carboxylic acid groups. The phenolic hydroxyl

groups exert the strongest effect. Because of the effect of pH on the dissociation of the phenolic groups, pH has a very marked effect on the stability of the alkali lignin. Concentration of the liquor can also tend to destabilize the lignin colloid, by decreasing electrostatic double layers and the protecting shell of water molecules. This effect is less marked than the effect of pH.

The resin acids and fatty acids which are present in the liquors as soaps associate to form micelles. The micelles are capable of solubilizing in their hydrophobic inner parts nonpolar compounds in the black liquor such as some extractives. The colloidal stability of the micelles is dependent on their electrical charge. It can be lowered by raising the salt concentration to a level high enough to suppress the electrical double layer. Normally the minimum solubility of the soaps is reached at liquor concentrations of 25 to 28% dissolved solids.

PROPOSAL OBJECTIVES

The specific objectives of the proposed program to study solubility limits in black liquor were as follows:

1. Determine the solubilities of the inorganic salts, Na_2CO_3, Na_2SO_4, and NaCl in black liquor as functions of temperature and concentration of other black liquor components.
2. Determine the conditions which lead to destabilization of the colloidal alkali lignin with particular attention paid to differences between hardwood and softwood lignin, pH, and the individual and total concentrations of the inorganic compounds.

3. Evaluate the extent of precipitation of salts of saccharinic and other organic acids and determine the saturation limits for those substances which do precipitate in black liquor.
4. Develop a procedure for using the solubility data obtained in the program to estimate the concentrations at which scaling would occur for a given liquor.
5. Evaluate the possibility of using simplified test methods to determine scaling limits.

In carrying out these objectives, the emphasis was placed on obtaining quantitative information and on generalizing the results to as large an extent as possible. Knowledge of solubility limits restricted to a single liquor was considered of limited value.

APPROACH

Equilibrium Solubility Data

The major objective of this program was to obtain basic solubility data on the liquor components of interest. In order to obtain valid solubility data, the system must be at equilibrium. All of the solubility data obtained in this study were obtained under equilibrium conditions.

The basic requirements in attaining equilibrium are a closed, constant temperature system and sufficient time for all precipitation and dissolution reactions to go to completion. This was accomplished by carrying out the solubility experiments in closed, stirred vessels immersed in a hot bath and allowing twenty-four hours for the system to equilibrate before sampling.

Precautions were taken to minimize temperature or concentration gradients which might affect the solubility data. The liquors were continually

stirred using a stirrer with a close clearance between the vessel walls and bottom so that precipitation and crystal growth would occur in the bulk rather than on the vessel walls. When it was necessary to concentrate a liquor, it was done in the vessels in the hot bath over a period of several hours using a small nitrogen purge to remove water vapor from the vessel. It was expected that all vaporization would occur at the free surface of liquor, and that there would thus be no boiling on the walls of the containing vessel. The temperature of the vessel wall would then be essentially the same as the liquor temperature. After a liquor was concentrated, an additional twenty-four hour equilibration time was allowed before sampling.

Saturation equilibrium conditions were approached in a number of ways in the course of this study. In some cases, an excess amount of the substance whose limits were being tested was added to black liquor and equilibrium approached by dissolution. In other cases, an unsaturated liquor was concentrated by slow, isothermal evaporation and equilibrium was approached by precipitation. A third technique was to add more soluble substances to liquor saturated with the substance under test and thus drive it from solution. If truly equilibrium conditions were obtained, the solubility data would be independent of the method of approach.

The second basic requirement in obtaining valid solubility data is to distinguish the true solution phase from the solid phase and determine the composition of each. This is normally straightforward in aqueous solutions, but can become complicated in black liquor. Green and Fratalli used fritted glass filters to obtain solution phase samples in their work on the solubility of Na_2CO_3-Na_2SO_4-NaOH in water. The same technique was adopted for use in this study. For black liquors, the solution phase was arbitrarily defined as that

which would pass through a coarse fritted glass filter (pore size 40-60 μm). Initial attempts were made to use medium or fine grades of fritted filters (pore sizes of 10-15 and about 5 μm, respectively) to minimize the risk of small crystalites passing through with the solution phase. However, these were much more impermeable to high solids black liquor, and it was impossible to get sufficient sample with the finer filters.

A good deal of difficulty was encountered in obtaining samples of the solid phase, since these are always contaminated with liquor. Initially, it was attempted to obtain solid samples by removing some of the liquor from the vessel bottom through a normal glass tube and filtering off the solids on a coarse filter. Cooling of the liquor during sample removal and the filtering attempt caused the liquor viscosity to increase greatly and render separation impossible. Direct analysis of the material removed in this manner was also unsuccessful because the amount of entrained liquor was too great and placed too much of a burden on the accuracy of composition data. The technique which was finally adopted was to allow some time for the solids to settle at the equilibrium temperature after the solution sample was taken, remove the vessels from the hot bath, and decant off the liquor. A sample of the sludge accumulated at the bottom of the vessel was then taken. No attempt was made to wash the residual liquor from the solid, because it was felt that the solids would be likely to redissolve during washing before the liquor could all be removed. Instead, the composition of the sludge was determined, and the composition of the true solid phase calculated from material balance and the composition of the solution phase. This procedure is directly analogous to Schreinemaker's rest method commonly used in aqueous solubility work.

Inorganic Salts

Determination of solubility limits for the inorganic salts Na_2CO_3, Na_2SO_4 and NaCl and $CaCO_3$ constituted a major part of this study. This was due not only to the role these materials play in evaporator scaling, but also to the fact that saturation concepts should be especially applicable to these substances, and they would thus provide insight into the nature of solubility phenomena in black liquor. A large amount of data on the mutual solubilities of these materials in water and of the effects of other inorganic salts on their solubilities exists and is available as a basis to interpret their solubility in black liquor. The work of Green and Fratalli (7) on the systems Na_2CO_3-NaOH-H_2O, Na_2SO_4-NaOH-H_2O, Na_2CO_3-Na_2SO_4-H_2O and Na_2CO_3-Na_2SO_4-NaOH-H_2O is fundamental to this interpretation. A very comprehensive set of solubility data is given by Seidell (9). This can be used to extend the work of Green and Fratalli and to interpret the effects of other salts such as NaCl, $Na_2S_2O_3$, etc.

In interpreting the solubility of inorganic salts in black liquor, the liquor is first considered as an aqueous solution. The amounts of inorganic salts are calculated relative to the amount of water in the liquor and these values compared with data from Green and Fratalli or Seidel. The effects of total sodium in the liquor as well as certain inorganics can then be determined in terms of the expected behavior in an aqueous solution. By varying the total solids content of the liquor, the effect of the organic content of the liquor can be examined. It was felt that by making use of the data on aqueous solutions, the black liquor solubility data could be generalized to cover a wide range of liquor variables. Deviations from the solubility expected from aqueous data would provide information on the nature of high solids black liquor.

Organics

It was expected that precipitation of organic materials would be more complex and the generalization of organic solubility data more difficult than that for inorganic salts. There are several reasons for this. The organic fraction of the black liquor is much more heterogeneous and, in many cases, can only be characterized into classes rather than specific compounds. The variation in the organic materials in the liquor from one mill to another would be expected to be much greater than the inorganic fraction. Another factor is that a portion of the organic system is colloidal and precipitation occurs by colloidal destabilization. These colloids are supposed to be stabilized by electrostatic charges and thus the stability is dependent on the degree of ionization of phenolic hydroxyls (hence, pH) and the effect of counterion concentration on the electrostatic double layer (total solids, inorganic ions). The interrelationships which would define a point of destabilization (solubility limit) could be very complex, and the limit could be diffuse. Another possibility of organic precipitation could be crystallization of the salts of saccharinic acids formed from the hemicelluloses.

In this study, the problem of organic precipitation was approached in the following manner. The major emphasis was placed on the extent of occurrence of organic precipitation. The main variable involved was the solids content of the liquor. The reversibility of dissolution and precipitation with respect to pH changes was also examined. Organics were normally determined by difference. Of the total liquor solids present, a part could be assigned to various inorganic salts such as Na_2CO_3 and Na_2SO_4. Of the total sodium in the black liquor, a part could be assigned to known inorganic salts and the remainder was assumed to be organically bound sodium. The difference between the total solids and the sum of known inorganics and organically bound sodium was considered to be "organics." This was the prime indication of the extent of organic precipitation.

EXPERIMENTAL

REQUIREMENTS

The basic requirements for the experimental system are set by the desire to obtain solubility data under equilibrium conditions and the need to obtain samples of the solution and solid phases. The philosophical aspects of these requirements were discussed earlier. From a practical point of view, they dictated the nature of the equipment employed.

The need for maintaining equilibrium conditions set several requirements as follows:

1. Experiments had to be carried out in an isothermal environment.
2. Continuous agitation of the liquor was needed to minimize heterogeneities and to enhance rates of precipitation or dilution.
3. The system had to be closed with respect to loss of volatiles from the liquor.
4. It was necessary for the system to operate for long periods (24 hours) without attendance.
5. Sampling had to be carried out without interfering with the equilibrium, especially if the liquor was under pressure.

As was explained earlier, solution phase samples were obtained using coarse, fritted glass filters. It was necessary to design the system so that samples could be taken from a pressurized liquor while also keeping the filter out of the liquor prior to sampling to avoid plugging. Since solid phase

samples were obtained by disassembling the apparatus and decanting off the liquor, no particular requirements were introduced on this score.

In addition to the need for thermodynamic equilibrium and satisfactory sampling, the success of a program such as this is very heavily dependent on the ability to make quantitative measurements on the composition of the liquors. The analytical requirements include the following:

1. Total solids content — This is the most important single quantity in the solubility data, because it determines the relative proportions of liquor solids and water.
2. Sodium salts — Quantitative data are required for Na_2CO_3, Na_2SO_4, NaOH, and NaCl, $Na_2S_2O_3$, and Na_2S on occasion. Total sodium determinations are used to find the amount of organically bound sodium. Total sulfur is also useful.
3. Calcium — Data on total calcium in the liquor are needed for determinations of solubilities of calcium salts. The analysis is complicated by the presence of large amounts of sodium in the samples.
4. Organics — As discussed previously, organics are determined basically as the difference between the total solids and the sum of the known inorganics and the organically bound sodium. If a further breakdown is desired, attempts to determine the proportions of ligneous, hemicellulose or resinous materials in the sample would be made.

The amount of analytical work required is the major determinant in the extent of the experimental work performed on this study. Ideally, on any given experiment there would be samples of the original liquor, several solution phase samples as a function of time to ensure that equilibrium is attained, and a contaminated solid phase sample. Each sample would then be subjected to a comprehensive set of analyses. Such a procedure would be prohibitive in this project where a wide range of liquor composition variables were to be examined. The minimum analytic requirements are for a single solution and single solid phase sample and would include only those measurements needed to define the composition of the "true" solid phase (as opposed to the contaminated sample) and the amounts of those components influencing the amounts in the solution phase. Most of the analytical work on this project approached this minimum. As a general rule, duplicate determinations were not run, in order to keep the analytical work within reasonable bounds.

DESCRIPTION OF SYSTEM

The basic experimental system consisted of five stainless steel stirred vessels, equipped with provisions for sampling, submerged in a constant temperature oil bath.

A diagram of one of the stirred vessels is shown in Fig. 1. The vessel is all stainless steel, 6 inches I.D. by 8 inches deep. A small hole is partially drilled through the bottom plate in the center to serve as a guide for the stirrer shaft. The stirrer is supported off the top plate. The stirrer shaft is 3/8-inch diameter stainless steel rod and the stirrer blades are 1 inch wide by 1/8-inch thick stainless. The blades are welded into an assembly so that one blade rides near the bottom and the other two

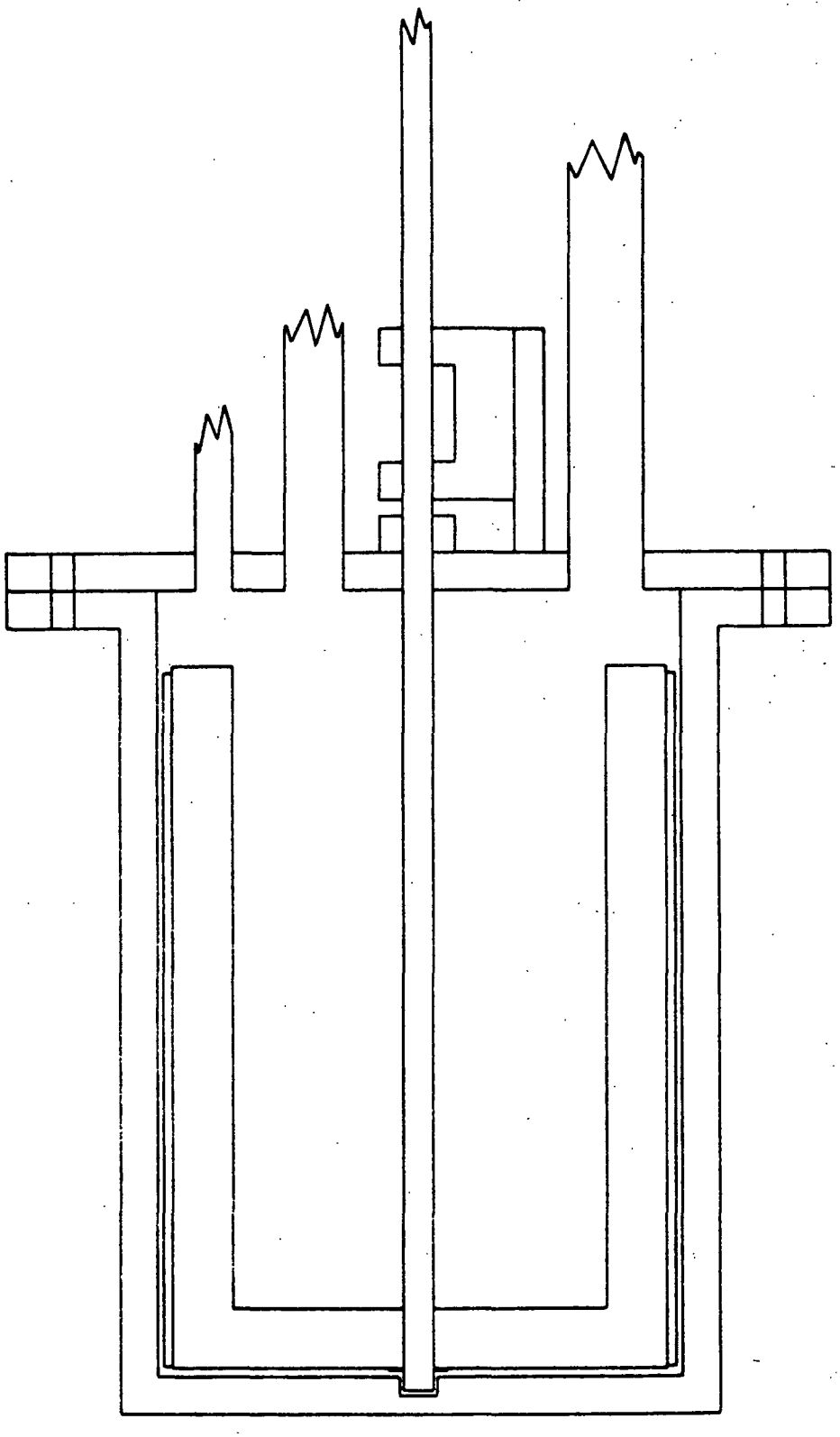


Figure 1. Diagram of Stirred Vessel

rise perpendicularly along the sides. A strip of teflon is attached to each of the side blades and rides on the sides of the vessel. There is no teflon strip along the bottom blade, and there is a small clearance between the bottom blade and the bottom of the vessel. The shaft of the stirrer passes through a packing gland to permit operation with some pressure within the vessel. The support bearings for the stirrer are attached to the top plate but on the outside of the vessel. The stirrer is coupled to the drive through a shear pin so that it automatically decouples if the stirrer should jam. The stirrer was rotated at about 60 rpm. Three pipes are also attached to the top plate. The smallest is used for pressurizing the system with N_2 and for providing the N_2 sweep during evaporation. The second is provided for adding materials to the vessel after it is assembled. The largest provides for the sampling probe. It is tall enough and wide enough to contain the fritted glass filter within it above the liquor in the vessel.

After an initial period of examining different sizes and types of fritted glass filter, a single type was selected for the remainder of the program. These were tubular filters of 5/8-inch diameter with a 4-inch fritted length. The porosity was coarse (40-60 μm). The tubular filter was attached to ordinary Pyrex capillary tubing. The capillary tube passed through a packing gland on the sampling pipe attached to the top plate of the reaction vessel. When a sample from a liquor at atmospheric pressure was required, the sampling pipe would simply be capped off during the equilibration period. Just prior to sampling, the fritted glass filter-capillary tube-packing gland assembly would be put on the sampling pipe, tightened, and liquor forced through the filter by applying N_2 pressure to the liquor in the vessel. When a sample at pressures above atmospheric was required, the sampling assembly

would be connected to the sampling pipe before heating the liquor and a stopcock was attached to the top of the capillary tube to seal the system. The fritted filter would be retracted so that it was enclosed entirely within the sampling pipe above the liquor. After the equilibration period, the packing gland on the capillary tube was loosened slightly and the filter forced down into the liquor. The stopcock was then opened and the sample taken. The high pressure sampling system is shown in Fig. 2.

One problem did occur with the use of the fritted glass filters to obtain samples of the solution phase. The glass was attacked by the alkaline liquors and even more strongly when caustic was added. This did not seem to cause any trouble with the solubility data. Green and Fratalli's data on Na_2SO_4-Na_2CO_3-NaOH in water were approached satisfactorily. There was no evidence of serious silicate contamination of the liquor samples. The main effect of the attack was a gradual embrittlement and eventual failure of the filters themselves. This made it necessary to use a relatively large number of filters and the program was delayed slightly in midstream due to the inability to get shipment of replacement filters.

Isothermal conditions were maintained by immersing the stirred vessels in a constant temperature oil bath. The bath was large enough to accommodate five reaction vessels. The heating elements were located external to the bath itself and hot oil was continuously recirculated through the bath. Normally, the temperature could be held within $\pm 2^{\circ}C$ during a twenty-four hour run. Temperatures were monitored continuously during the early part of this work until it was established that the control system was working. A thermometer was used for most of the study. A fixture was placed within the bath to support each of the five vessels in a fixed

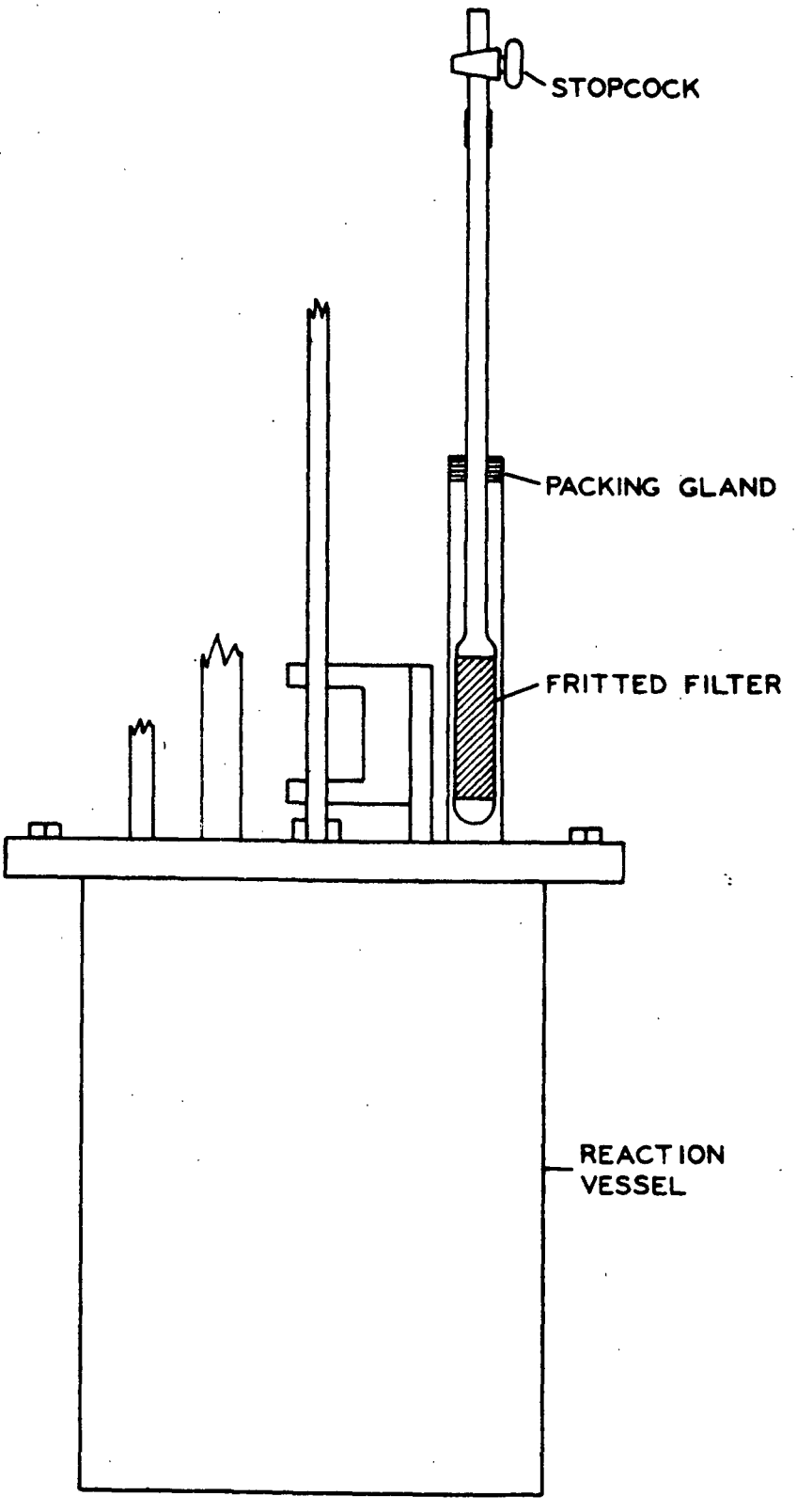


Figure 2. Schematic of Pressurized Sampling System

position. The drive mechanism for the stirrers was attached to a frame extending over the hot bath. A small pump was used to transfer oil between the bath and a storage tank. This permitted relatively rapid removal of the vessels from the system for solid sampling after solution samples were taken.

Each of the vessels were connected to a manifold which in turn was connected to a nitrogen cylinder and a pressure gage. A valve was located between the manifold and each vessel and another valve between the N_2 cylinder and the manifold. This permitted any given vessel to be isolated or connected to the pressurization or purge nitrogen. When all the valves were open, this did provide a cross connection between the vessels, so that if a leak occurred in any part of the system during a run at temperature above the normal boiling point, the liquor in each vessel would boil and vent through the manifold and out the leak.

PROCEDURES

It was found that the vessels had to be assembled before being loaded with black liquor. This was necessary to ensure that the stirrer properly fit into the guide at the bottom of the vessel and to minimize the possibility of trapping particulates in the guide. The vessels were loaded quantitatively to provide the opportunity to carry out material balances over the experimental run. This included introducing known amounts of black liquor, inorganic additives and water into the vessel. The addition of known amounts of liquor caused some problems because of the high viscosity of black liquor and its tendency to cling to the walls of transfer vessels. Two procedures were used. The most common was to tare the empty vessel on a balance and then add liquor until the weight of vessel and liquor had increased by the desired amount. When the amount of liquor to be added was greater than the capacity of the vessel (at

the initial solids content), a portion of the liquor was added by the above method. The remainder was added to the vessel while in the hot bath and the quantity added by weighing the transfer vessel before and after addition.

If it was necessary to concentrate the liquors to reach a desired solids content, this was carried out in the hot bath at a temperature of about 100°C. A glass condenser was attached to the sampling pipe so that the amount of water evaporated could be measured. The liquor would be stirred in the usual manner while the evaporation was proceeding. A small purge flow of nitrogen was used to sweep water vapor from the vessels. The evaporation was carried out slowly over a period of several hours. It was attempted to have the evaporation take place at the free surface rather than by boiling on the vessel walls. Liquors would be added at intervals during the course of the concentration, and the total amounts of liquor added and condensate formed kept track of.

In many experiments, certain inorganic substances were added to the liquor in the vessels. These included such materials as Na_2CO_3, Na_2SO_4, NaCl, and NaOH. These substances were also added quantitatively. This was done in either of two ways. The first method was to add the material as a dry solid to the liquor as it was being stirred in the vessels. The second method was to first form a solution of known concentration from the substance and then add the solution to the liquor in the pot. The desired amount of water would then be removed by concentration. Both of these methods were used successfully in this program.

After all of the desired materials were placed in the vessels and the solids content brought to the required level, the system would be allowed to equilibrate. This was done by continuing to stir the liquor at the desired

temperature level and avoiding disturbances for a specified time period. Normally, this time period was about twenty-four hours. The system would be left overnight after being brought to the desired condition with sampling occurring the next morning. The minimum equilibration time in these studies was 18 to 20 hours.

Sampling

Solution samples were obtained with the fritted glass filters as described above. The procedure varied somewhat depending on whether or not the pressure in the vessels was above atmospheric. If there was no excess pressure in the vessel, the sampling assembly would be attached just prior to the sampling time. Nitrogen pressure would then be applied to force liquor through the filter and up the capillary tube. If the pressure was above atmospheric, the sampling assembly would be attached prior to the equilibration period and a stopcock added to the end of the capillary tube as a seal. The filter would be held up in the sampling pipe above the liquor until just before the sampling period. Then the probe would be forced into the liquor, the stopcock opened and the sample taken.

It was necessary to stop the stirrers when taking solution samples to avoid striking the filters with the stirrer blades. In most cases, all five vessels were sampled at about the same time and the stirrer drive would simply be shut off. If only a single vessel was to be sampled, the drive would be stopped, the individual stirrer disconnected, and the drive restarted.

The solution samples were caught in small glass weighing bottles. Immediately after the sample was taken, the bottles would be covered to prevent loss of moisture. After cooling, the bottles were weighed to determine the total amount of sample taken. The samples were then diluted up to a known

volume, usually 250 ml. Measurement of the density and total solids of the dilute sample along with the sample weight allowed a direct calculation of the solids content of the original solids.

$$\% \text{ original solids} = \frac{\text{density x dilute volume x \% dilute solids}}{\text{weight of original sample}}$$

All analytical tests for composition were carried out on the diluted sample and expressed relative to the solids present (i.e., % on solids). This procedure was used because it was normally difficult to obtain a sample greater than 20 to 30 ml, and the dilution technique was very convenient to use.

Solid samples were obtained by decanting off the liquor. After solution samples were obtained, the bath heaters would be shut off and the oil pumped to the storage barrel. The vessel would then be soaked in Gunk and hosed down to remove the remaining oil to permit handling. The top plate and its assembly would then be removed and the liquor in the vessel slowly poured into the sink. As the sludge on the bottom of the vessels slowly became uncovered, periodic samples would be taken and put in a weighing bottle. In this way, a cumulative sample of the sludge would be built up. Typically, a 25 to 50 g sludge sample would be obtained. This was then weighed and diluted (normally to 500 ml) in the same manner as solution samples.

It was recognized that there were some serious potential problems in this method of obtaining solid phase samples because it is a nonequilibrium procedure and the liquor has a possibility to cool. However, it was felt to be the best procedure available considering analytical requirements and time. It seems likely that crystallization processes in the black liquor would be relatively slow so that the sludge would be more representative of the earlier equilibrium conditions than those prevailing when the sample was actually taken.

In addition, the solid phase composition is less critical to the determination of solubility limits than the solution phase composition.

Analytical Procedures

Samples were analyzed for total solids, total sodium, total sulfur, Na_2CO_3, Na_2SO_4, active alkali, NaCl, $Na_2S_2O_3$, Na_2S and calcium. Organic was normally determined by difference. Special procedures for organics will be described where relevant.

Solids content of the black liquors was determined in accordance with TAPPI Procedure T 650 su-71. This involves oven drying at 105°C and the use of an inert surface extender.

Sodium carbonate (Na_2CO_3) was determined by a CO_2 evolution procedure. This procedure treats a weighed liquor sample with acid and measures the carbon dioxide released by absorbing it on ascarite. It is described in TAPPI Procedure T 624 os-68.

Sodium sulfate (Na_2SO_4) was determined by precipitation as $BaSO_4$ according to TAPPI Procedure T 625 ts-63.

Active alkali (actually NaOH, Na_2S and all other strongly alkaline salts) was determined by titration of a liquor sample with HCl down to pH 8.3 followed by correction for the Na_2CO_3 present as determined by the CO_2 evolution procedure. Expressed as Na_2O.

Total sodium was determined by flame ionization spectrophotometry after digestion of the sample with perchloric acid as described in T 625 ts-63.

Total sulfur was found by precipitation as $BaSO_4$ after perchloric acid digestion as described in T 625 ts-63.

Sodium chloride was found by a Volkard procedure on a sample which was dried and ashed.

Sodium sulfide was determined with a special sulfide ion specific electrode.

Sodium thiosulfate was determined with a mercury pool electrode as described in T 625 ts-63.

Calcium was found by EDTA titration and by atomic absorption spectroscopy on perchloric acid-digested samples.

Liquors Used

Black liquors used in this study were all obtained from operating kraft mills of sponsoring companies. The mills from which liquors were solicited were selected to provide a broad range of variables which were felt to be important. These included a wide geographical spread, varying proportions of hardwood and softwood, and inclusion of semichemical liquor in some cases. Liquors from nine different mills were obtained and used in the program. These liquors are coded and described in Appendix I.

The liquors were shipped to the Institute in barrels or other large containers. They were stored in a large cold room after taking samples for analysis. Removing liquors from the large drums was quite difficult and there was some tendency for solids to slowly settle out during storage, so four gallon plastic pails, with covers, were used for intermediate storage. Periodically the smaller pails would be filled from the drums. Liquor for the test vessels was always taken from the plastic pails. Due to the settling of material in the large drums, and possible slow chemical reactions in the liquor, the composition of a given liquid did not remain completely constant during the full course of the program.

DATA ANALYSIS

PHASE COMPOSITION

The basic requirement in a solubility study is data on the composition of the solution phase and the solid phase which are in equilibrium with each other. In applying these concepts to black liquor, it is tacitly assumed that black liquor can be treated as an aqueous solution. While this is undoubtedly valid for weak liquors at 20% solids concentration, it is less obvious that it remains true at 65% solids content. In this study, the solution phase is defined in a purely operational manner as that part of the liquor system which passes through a fritted glass filter of coarse porosity. On this basis, the solid phase would then be that portion of the liquor system which does not pass through the filter. However, the operational definition of the solid phase is determined by the method of obtaining the solid phase sample. Thus, in this study, the solid phase is defined from analysis of the sludge sample after correction for the solution phase entrained in the sample. If the concept of equilibrium between a true solution and a true solid is valid, if the filter does in fact pass only the solution phase, and if the composition of the solid phase does not change significantly during the process of obtaining the solid phase (sludge) sample, then the phases defined operationally in this study will be identical with the true solution and solid phases. It is believed that this is generally the case. Overall material balances provide a check on this assumption.

The composition of the solution phase is determined directly from analysis of the solution phase sample. The total solids content of the sample is calculated as described above, and the detailed composition is expressed as the weight percentages of the various components on the solids.

The determination of the composition of the solid phase is complicated by the inability to obtain a clean sample of the solid phase. The sludge sample which is taken contains a varying proportion of solution phase which must be accounted for. Another potential problem is the possibility of different crystal forms due to different degrees of hydration. The substances forming solid phase in this study were not expected to form hydrates at temperatures of 100°C or above, so hydrate formation was discounted in calculating the composition of the solid phase. The composition of the solid phase was calculated by material balance assuming that all of the water in the sludge sample is associated with entrained solution phase. The sludge sample is assumed to contain a weight fraction, f, of true solid phase with the remainder solution phase. By material balance,

$$f = \frac{Y_S - Y_L}{1 - Y_L} \qquad (1)$$

where

Y_S = solids content of sludge sample, g/g sample

Y_L = solids content of solution sample, g/g sample

A separate material balance is carried out for each component desired, to obtain the fraction of that component in the true solid phase. This results in the equation:

$$X_{TS} = \frac{X_S Y_S - (1-f)\, X_L Y_L}{f} \qquad (2)$$

where

X_{TS} = weight fraction component A in true solids, g/g solids

X_S = weight fraction component A in sludge sample, g/g solids

X_L = weight fraction component A in solution sample, g/g solids

By employing these equations operating on the composition data for the solution sample and the sludge sample, the composition of the true solid phase can be calculated. This procedure is basically the same as Schreinemakers' rest method as used by Green and Fratalli and others, except for the tacit assumption that no hydrates are formed.

This procedure is highly sensitive to the accuracy of the analytical data on the samples, and on the total solids determination in particular. This is especially true when the solids content of the sludge sample is close to the solids content of the solution phase. (This can occur when there is little solid phase in the system.) In this case, f becomes small and the numerator in Equation (2) is a small difference between two large numbers.

A built-in check on the accuracy of the data normally does exist in this procedure. The strong alkalies in the black liquor (determined as Na_2O as described in the previous section but actually consisting of NaOH, Na_2S and possibly some sodium organic compounds) would be expected to be soluble under all conditions that black liquor is normally exposed to. Thus, one check on the data is to determine if the "Na_2O" calculated for the true solid is negligible. In most cases, this was found to be the case.

The components of the liquor which were directly determined by analysis were total solids and most of the inorganic. The organic fraction was determined by difference. There is a certain arbitrariness to this procedure because the borderline between organic and inorganic can become rather hazy in certain circumstances and a completely rigorous description of the inorganics was not obtained in all circumstances. In most of the runs, thiosulfate and sulfide were not determined, since these were time-consuming analyses

to run and they were very soluble species. This does, however, cause a problem in defining the organic content in the liquor. In the ideal case, the organic would be defined as follows:

$$\text{organic} = 100 - Na_2CO_3 - Na_2SO_4 - NaOH - Na_2S - Na_2S_2O_3 - NaCl - \text{organic sodium.}$$

$$\text{organic sodium} = \text{total sodium} - 23 \times \frac{Na_2CO_3}{53} + \frac{Na_2SO_4}{71} + \frac{NaOH}{40} + \frac{Na_2S}{39} + \frac{Na_2S_2O_3}{79} + \frac{NaCl}{58.5}$$

In the case where Na_2S and $Na_2S_2O_3$ are not directly determined, use may be made of the relations:

$$\frac{\text{total sulfur}}{32} = \frac{Na_2SO_4}{142} + \frac{Na_2S}{78} + \frac{Na_2S_2O_3}{79}$$

and

$$Na_2O = \frac{31}{40} NaOH + \frac{31}{39} Na_2S$$

substituting these into the relations for % organic and organic sodium gives:

$$\text{organic} = 100 - \text{total sodium} - \frac{7}{4} \text{total sulfur} - \frac{30}{53} Na_2CO_3 - \frac{20}{71} Na_2SO_4 - \frac{17}{31} Na_2O - \frac{35.5}{58.5} NaCl + \frac{29}{39} Na_2S$$

The only uncertainty would be with the amount of Na_2S. However, this can be bounded, since it is known that:

$$Na_2S \leq \frac{39}{31} Na_2O$$

and

$$Na_2S \leq \frac{39}{16} \text{total sulfur} - \frac{39}{71} Na_2SO_4$$

Material Balances

Material balances can be applied to each of the solubility experiments to serve as a check on the accuracy of the solubility data obtained. They also provide an alternative to the direct determination of the composition of the solid phase. The concept of the material balance is quite simple in this situation. If the system is truly closed, all of the liquor solids must appear as either solution phase or solid phase. Thus, the sum of the total amount of a material in the solution phase and in the solid phase should equal the total amount of that material in the system. This check can be made for each component as desired.

The formulation of the material balance begins with knowledge of the inputs to the reaction vessels. This includes the total amount of liquor introduced into the vessels, the solids content of the liquor, and the detailed composition of the liquor solids. It also requires knowing the amounts of inorganic chemicals added to the liquor and the amount of water evaporated, if any. The accuracy of the material balance is no better than the accuracy of these input data.

Some assumption must be made about at least one component in order to calculate the amount of solid phase present. If no limitations are placed on the distributions of any of the components, the material balance becomes indeterminate. There are a number of assumptions which can be made and they each give a somewhat different material balance. Perhaps the most straightforward procedure is to make the same assumption as is made in calculating the composition of the solid phase, namely, that all water is associated with the solution phase. Then the total amount of water added to the vessels, minus that known to be evaporated is assumed to be present as solution phase, and this value and the measured solids content of the solution phase sample

is used to calculate the amount of solution phase in the system. The total amount of solid phase in the system can then be determined by difference on a solids balance. This procedure was not normally the most successful, because accurate knowledge of the total amount of water in the system is not always available. Accuracy is required on two measurements, the total amount of water initially put into the vessels (as liquor and inorganic solutions) and the amount of water evaporated. In addition, some water could slowly leak out of the vessel at the stirrer seal during the equilibration period.

Alternative methods for formulating material balances were used in the course of the work. One possibility was to use the strong alkalies, determined as Na_2O, and assume that they remained with the solution phase. (This assumption agrees very well with calculations of the solid phase composition based on analysis of solution and sludge samples.) However, these strong alkalies are a minor component of the liquor solids (less than 10%) and their use as the tie element in the material balance placed an unreasonable demand on the accuracy of the analyses. Consequently, this technique did not meet with too much success.

The most satisfactory method for formulating material balances was to assume conservation of the sum of Na_2CO_3 and Na_2SO_4. Balances run in this manner were especially useful in estimating the amounts of these inorganics remaining as solid phase and, thus, indicating when saturation was only marginally established.

Sample material balances are given in Appendix III. All material balances which are relevant to the proper interpretation of the results are given in this Appendix.

EXPERIMENTAL PROGRAM

Solubility experiments which were carried out in the course of this program can be divided into four categories, according to the main objective of the experiment. These were screening experiments, studies of the solubilities of Na_2CO_3 and Na_2SO_4, an experiment on $CaCO_3$ solubility, and experiments concerned with the solubility and colloidal stability of the organics.

The screening experiments were of a preliminary nature and were designed to check out the validity of the experimental system and to orient the solubility study to those components of greatest importance in black liquor systems. The initial experiment was concerned with purely inorganic systems involving Na_2CO_3, Na_2SO_4, NaCl and NaOH, in order to check solubilities determined by these procedures against published values. A second experiment was carried out using Na_2SO_4, Na_2CO_3 and a soda liquor which was available in order to check out techniques on black liquor. A third experiment was concerned with characterizing the liquors which were obtained from the mills and the nature of the material precipitated from them when they were concentrated to high solids.

A major part of the program was devoted to the study of the solubility limits of Na_2CO_3 and Na_2SO_4 in black liquors and the variables affecting these limits. Data were obtained on the solubilities of Na_2CO_3 and Na_2SO_4 in each of the mill liquors used in the program. Variables examined included the effects of NaCl, $Na_2S_2O_3$, and NaOH on the solubilities of Na_2CO_3/Na_2SO_4, temperature and total solids content of the liquors. This part of the study received major attention not only because of the importance of Na_2CO_3/Na_2SO_4 scaling problems, but also because it was felt possible to bring this part to

definitive conclusions. Sodium carbonate and sodium sulfate were the only sodium salts which were found to precipitate to any appreciable extent during the course of this study. Other sodium salts such as NaCl, $Na_2S_2O_3$, Na_2S and NaOH were quite soluble in black liquor.

One experiment was carried out to determine the solubility of $CaCO_3$ in black liquors. Although this was not specifically mentioned in the proposal, it was undertaken because of the role that $CaCO_3$ can play in evaporator scaling, and to determine if some of the liquor organics could complex and solubilize significant amounts of calcium.

A number of experiments were carried out to study the solubility of organic components in the liquors. Because of the nature of the organics in black liquor, this could not be approached in the same manner as the solubility of inorganic substances. It was necessary, instead, to carry out certain operations on the liquor and observe what happened to the organics. These included concentrating the liquors to high solids, prolonged exposure of high solids liquor to high temperature, changes in liquor pH, and addition of inorganic substances.

A brief summary of the objectives and procedures for each experiment is given in Table I. Detailed descriptions of the experiments and tabulations of the solubility data obtained from them are given in Appendix II. All experiments were carried out at 100°C unless otherwise noted.

TABLE I

SUMMARY OF OBJECTIVES AND PROCEDURES FOR
EXPERIMENTS CARRIED OUT IN PROGRAM

Experiment 1: The objective of this experiment was to check out the experimental procedures using inorganic solutions with known solubility limits. Solubilities of Na_2CO_3, Na_2SO_4 and NaCl in water were determined as functions of NaOH addition and equilibration time.

Experiment 2: The purpose of this experiment was to check out sampling and analysis procedures with black liquor. Solubilities of Na_2CO_3 and Na_2SO_4 in a soda liquor were determined. Various methods of obtaining sludge (solid phase) samples were examined.

Experiment 3: The purpose of this experiment was to characterize the various black liquors obtained from the mills and determine what materials would precipitate from each liquor upon concentration to high solids. Samples of the black liquors were taken and analyzed. Liquors were concentrated by evaporation in the stirred vessels to high solids (58-70%) and solution and solid samples taken.

Experiment 4: The objective of this experiment was to determine the influence of liquor composition on the solubilities of Na_2CO_3 and Na_2SO_4 at a fixed total solids content. Varying amounts of solid Na_2CO_3 and Na_2SO_4 were added to the liquors at 45% total solids, the system equilibrated and samples taken.

Experiment 5: The purpose of this experiment was to examine the effect of liquor total solids content on the solubilities of Na_2CO_3 and Na_2SO_4. Solid Na_2CO_3 and Na_2SO_4 were added to two of the liquors at solids contents of 40, 45, 50, 55, and 60%.

TABLE I (Continued)

SUMMARY OF OBJECTIVES AND PROCEDURES FOR
EXPERIMENTS CARRIED OUT IN PROGRAM

Experiment 6: The objective of this experiment was to determine the effect of a neutral salt (NaCl) on the solubilities of Na_2CO_3 and Na_2SO_4 in black liquor. Sodium chloride was added to five different spent liquors at a total solids content of 55%. Two levels of salt addition were used for each. The NaCl was added as a 25% aqueous solution and the water evaporated off in the stirred vessels.

Experiment 7: The objective of this experiment was to determine the effect of $Na_2S_2O_3$ on the solubility of Na_2SO_4 and Na_2CO_3 in black liquors. A 25% aqueous solution of sodium thiosulfate was added to four different liquors and the concentration brought to 55-60% solids.

Experiment 8: The objective of this experiment was to examine the effect of temperature on the solubility of Na_2CO_3 and Na_2SO_4 in black liquor. A 20% aqueous solution of Na_2CO_3 and Na_2SO_4 was added to 5 black liquors and the concentration adjusted to about 47% solids. These were equilibrated at 120°C and then sampled in the usual manner.

Experiment 9: The purpose of this experiment was to extend the solubility data on Na_2CO_3/Na_2SO_4 in black liquors to 140°C, and to determine if a twenty-four hour exposure to these temperatures would increase the amount of precipitated organics.

Experiment 10: The objective of this experiment was to obtain some data on the solubility of $CaCO_3$ in black liquors and to examine the effect of liquor composition on these limits. Solid $CaCO_3$ was added to each of the liquors, and the systems equilibrated and sampled.

TABLE I (Continued)

SUMMARY OF OBJECTIVES AND PROCEDURES FOR
EXPERIMENTS CARRIED OUT IN PROGRAM

Experiment 11: The objective of this experiment was to obtain data on the composition of a sample of evaporator scale and of liquors from that evaporator to provide information on the relation between the solubility limits found in this study and sealing of evaporators. Samples of liquors and scale were obtained and analyzed.

Experiment 12: The objective of this experiment was to obtain solubility data under conditions considered most likely to lead to organic precipitation in evaporators. Five different liquors were concentrated to 65-70% solids and then held at 120°C for a minimum of twenty-four hours. Solution and solid phase samples were then taken in the usual manner.

Experiment 13: The objectives of this experiment were to see if the addition of NaOH to black liquors would reduce the solubility of Na_2CO_3 and Na_2SO_4 in the manner expected, and to determine the effect of NaOH addition on organic precipitation. Five different liquors, to which a 50% NaOH solution had been added, were concentrated to 60% solids, equilibrated and sampled.

Experiment 14: The objective of this experiment was to examine the effect of pH on the solubility of organic material in the liquor and to evaluate the reversibility of precipitation phenomena due to pH changes. Five different liquors were treated with HCl to cause a major lowering of pH, equilibrated and sampled. Sufficient NaOH was then added to neutralize the HCl added, the liquors equilibrated and then sampled again. One liquor was "titrated" with HCl and the viscosity determined as a function of acid addition.

TABLE I (Continued)

SUMMARY OF OBJECTIVES AND PROCEDURES FOR
EXPERIMENTS CARRIED OUT IN PROGRAM

Experiment 15: The objective of this experiment was to attempt to gain some understanding of why the solubilities of Na_2CO_3 and Na_2SO_4 is relatively greater in high solids liquors than would be expected based on their solubilities in water. Solubilities of Na_2CO_3 and Na_2SO_4 were determined in a very high solids sucrose solution, a lignin-rich liquor, and a lignin-poor liquor.

SOLUBILITIES OF Na_2CO_3 AND Na_2SO_4

GREEN AND FRATALLI'S DATA

In order to have a basis for understanding the solubilities of sodium carbonate and sodium sulfate in black liquor, it is necessary to examine their solubilities in water and in caustic solutions. The classic solubility study on the system Na_2CO_3-Na_2SO_4-NaOH-H_2O at 100°C was carried out by Green and Frattali (7). As part of that work, they also studied the relevant three component systems Na_2CO_3-NaOH-H_2O, Na_2SO_4-NaOH-H_2O and Na_2CO_3-Na_2SO_4-H_2O. The data on the four component system and on sulfate-carbonate-water are most relevant to the black liquor system.

Carbonate-Sulfate

Solubility data for the system Na_2CO_3-Na_2SO_4-H_2O at 100°C are shown in Fig. 3. This diagram also shows the application of Schreinemakers' rest method to the determination of the composition of the solid phase. The solubility behavior in this system can be divided into five distinct regions as follows:

1. A region in which a saturated solution is in equilibrium with solid $Na_2CO_3 \cdot H_2O$. The solution is rich in Na_2CO_3 and weak in Na_2SO_4. The proportions can vary slightly. This is represented by the left-handed branch of the equilibrium curve in Fig. 3.
2. A carbonate rich solution of fixed composition (28.6% Na_2CO_3, 3.4% Na_2SO_4, 68% H_2O) which is in equilibrium with two distinct solid phases. One phase is $Na_2CO_3 \cdot H_2O$ and the other is a solid solution having the composition

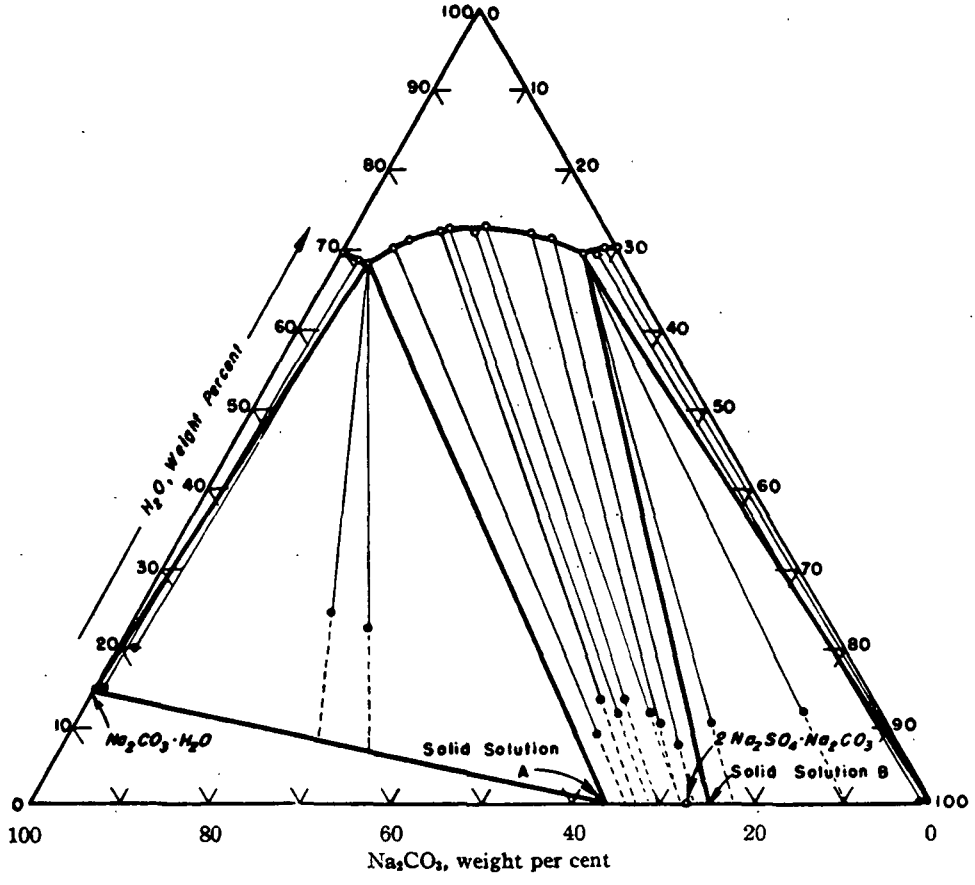


Figure 3. Solubility Diagram for Na_2CO_3-Na_2SO_4-H_2O from Green and Frattali (9)
O, Saturated Solution; C, Wet Residues

1.4 $Na_2SO_4 \cdot Na_2CO_3$. The solution of fixed composition represents an invariant point on the solubility diagram. It is found at the intersection of the left and middle branches of the solubility curve.

3. A region covering the widest range of solution compositions in which the saturated solution is in equilibrium with a solid solution of varying composition approximating that of burkeite ($2Na_2SO_4 \cdot Na_2CO_3$) and having a range in composition from 1.4 $Na_2SO_4 \cdot Na_2CO_3$ to 2.2 $Na_2SO_4 \cdot Na_2CO_3$. In this region, there is a one-to-one

correspondence between any particular solution composition and a solid phase composition. This region is given by the middle branch of the solubility curve.

4. A sulfate rich solution of fixed composition (4.1% Na_2CO_3, 26.5% Na_2SO_4, 69.4% H_2O) which is in equilibrium with two distinct solid phases. The first is a solid solution having the composition 2.2 $Na_2SO_4 \cdot Na_2CO_3$, and the second is anhydrous Na_2SO_4. The solution of fixed composition is an invariant point and is represented by the junction of the middle and right-hand branches of the solubility curve.
5. A region in which a sulfate rich saturated solution is in equilibrium with anhydrous Na_2SO_4. The composition of the saturated solution can vary slightly. This region is given as the right-hand branch of the solubility curve.

There are two basic pieces of information given by this diagram. These are the amounts of sulfate and carbonate which can dissolve in water, and the nature of the solid phase and the relation between the compositions of the solution and solid phases. This latter information is quite important to the interpretation of solubility data in black liquors. The relationships between solution phase composition and solid phase composition expressed in Fig. 3 are replotted in a more direct form in Fig. 4.

Figure 4 clearly shows the five distinct regions which were discussed above, the regions where the solid phase consists only of Na_2CO_3 or Na_2SO_4, the invariant points where the solid phase composition can change over a wide range

at fixed solution composition, and the important middle region where a linear relationship exists between the solution and solid compositions. Most importantly, this figure clearly demonstrates that a distinct monotonic functional relationship exists between the proportions of Na_2CO_3 and Na_2SO_4 in the solution and solid phases.

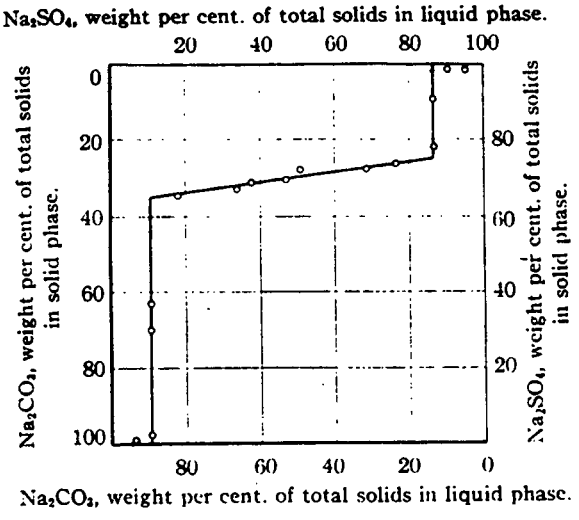


Figure 4. Phase Distribution Data for Na_2CO_3-Na_2SO_4-H_2O from Green and Frattali (9)

The main features of this Na_2CO_3-Na_2SO_4-H_2O system are that there are five distinct regions, and that the widest range of solution compositions are in equilibrium with a solid solution of Na_2CO_3 and Na_2SO_4 approximating burkeite in composition. Carbonate and sulfate tend to drive each other from solution on nearly a constant weight basis. The fraction of the system which is water is close to 70% over the full range. The significance of the invariant points is that the solution composition will move toward the invariant points as precipitation occurs.

Carbonate-Sulfate-Hydroxide

In this system, the hydroxide remains soluble and the substances which precipitate are carbonate and sulfate. The presence of hydroxide does have a marked effect on the solubilities of Na_2CO_3 and Na_2SO_4. This is a four-component system, Na_2CO_3-Na_2SO_4-NaOH-H_2O and as such is more difficult to represent on a two-dimensional plot. In addition, the introduction of another component (NaOH) without the introduction of more phases introduces an additional degree of freedom into the system. Saturation limits cannot be defined by a single solubility curve as was the case in the simpler Na_2CO_3-Na_2SO_4-H_2O system.

The solubility data of Green and Frattali for the carbonate-sulfate-hydroxide-water (C-S-H-W) system are presented in Table II and shown in Fig. 5. The data shown in Table II are for the univariant lines only. These data, along with the data for the relevant 3-component systems, were used to construct the triangular diagram given in Fig. 5. The ordinates of this diagram are the weight percentages of the three soluble components relative to each other. All points on the diagram represent solutions saturated with respect to a particular solid phase. The three corners of the diagram indicate saturated solutions of the individual salts, while the three sides represent the related three-component systems Na_2CO_3-Na_2SO_4-H_2O, Na_2CO_3-NaOH-H_2O and Na_2SO_4-NaOH-H_2O. The compression of information involved in Fig. 5 must be borne in mind. All of the solubility information given in Fig. 3 on the carbonate-sulfate system is now confined to the right-hand side of the triangle. The two invariant points in Fig. 3 are, thus, seen to correspond to the intersection of the two univariant lines with the NaOH = 0 axis.

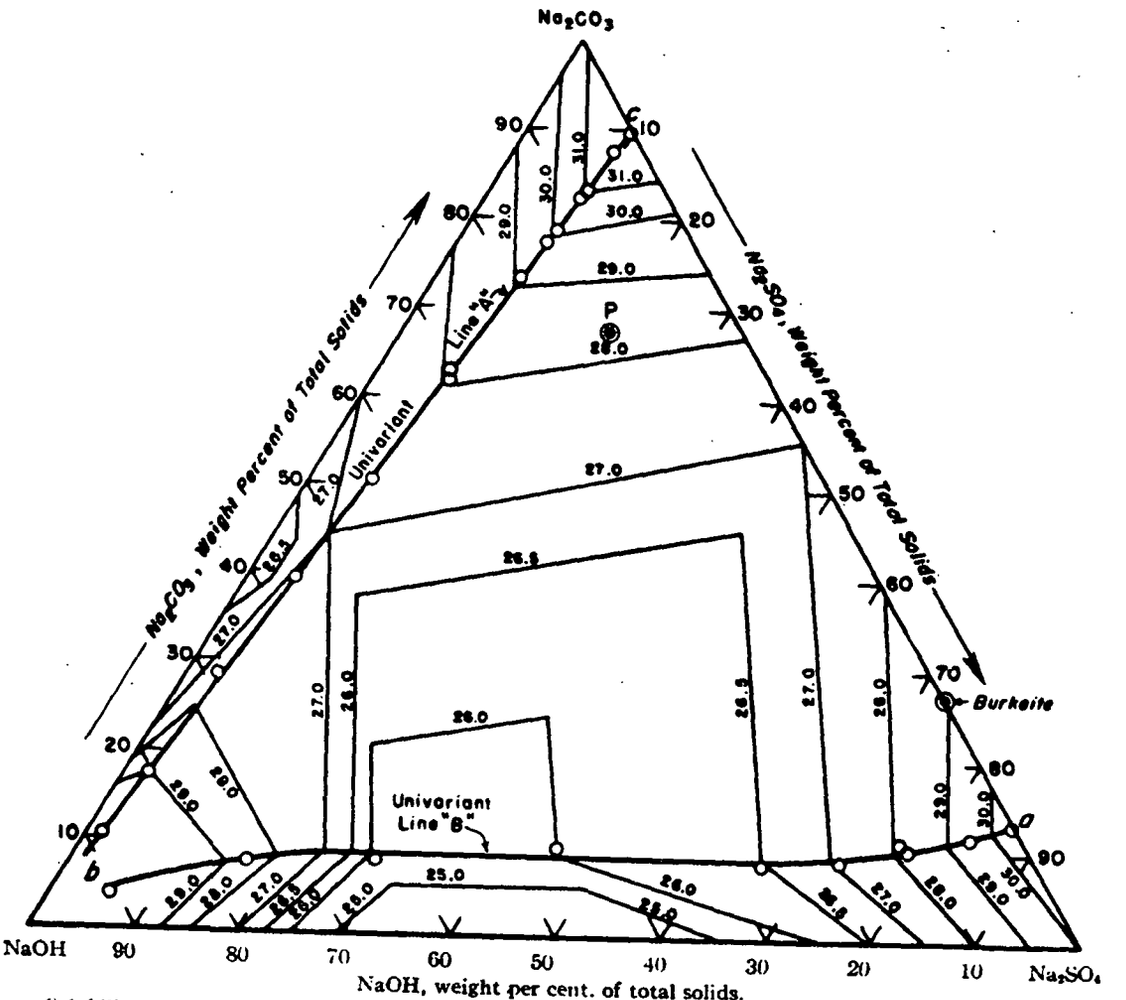
According to Green and Frattali, the solid phases involved in the four-component system are the same as those in the sulfate-carbonate system.

TABLE II

THE SYSTEM Na_2CO_3-Na_2SO_4-NaOH-H_2O AT 100°C

Soln.	Solution Composition, wt. %			Wet Residue Composition, wt. %			Solid Phase Identification, solid solution
	Na_2CO_3	Na_2SO_4	NaOH	Na_2CO_3	Na_2SO_4	NaOH[a]	
				Univariant Line A			
1	28.5	3.2	0	49.8	37.3	0	$Na_2CO_3 \cdot H_2O$
2	28.0	3.1	0.9	53.5	24.5	1.0	$Na_2CO_3 \cdot H_2O$
3	26.4	2.9	2.5	54.6	22.0	2.5	$Na_2CO_3 \cdot H_2O$
4	25.4	2.8	2.6	61.6	23.8	0	$Na_2CO_3 \cdot H_2O$
5	23.3	2.6	4.2	--	--	--	$Na_2CO_3 \cdot H_2O$
6[b]	23.8	2.5	3.8	62.6	18.4	0.9	$Na_2CO_3 \cdot H_2O$
7	21.5	2.3	5.4	56.9	16.8	2.3	$Na_2CO_3 \cdot H_2O$
8	17.9	1.9	8.6	67.1	13.6	0.6	$Na_2CO_3 \cdot H_2O$
9	17.4	2.0	8.7	61.5	15.3	1.6	$Na_2CO_3 \cdot H_2O$
10	14.0	1.7	12.0	68.7	12.6	0	$Na_2CO_3 \cdot H_2O$
11	10.8	1.2	15.4	--	--	--	$Na_2CO_3 \cdot H_2O$
12	8.0	0.8	18.9	55.2	8.3	0.2	$Na_2CO_3 \cdot H_2O$
13	5.0	0.6	23.2	50.9	7.1	9.2	$Na_2CO_3 \cdot H_2O$
14	3.2	0.5	26.9	51.9	6.8	11.0	$Na_2CO_3 \cdot H_2O$
				Univariant Line B			
1	4.0	26.6	0	19.3	70.5	0	Na_2SO_4
2	3.4	24.5	1.5	18.3	71.8	1.8	Na_2SO_4
3	3.0	21.8	3.4	--	--	--	--
4[c]	2.9	21.9	3.3	15.2	84.8	0	Na_2SO_4
5	2.4	19.6	5.1	15.3	78.8	0	Na_2SO_4
6	2.2	17.3	7.0	12.9	79.7	0.4	Na_2SO_4
7	2.5	11.7	11.8	--	--	--	Na_2SO_4
8	2.1	7.5	16.3	12.0	73.5	0.2	Na_2SO_4
9	2.3	4.7	21.4	12.9	71.9	2.6	Na_2SO_4
10	1.3	2.0	30.4	11.0	65.6	8.0	Na_2SO_4

[a] NaOH calculated by difference.
[b] Solution 5 given 68 hours agitation time, all others 20 hours.
[c] Solution 3 given 68 hours agitation time, all others 20 hours.



—Solubility curves for the system Na_2CO_3–Na_2SO_4–NaOH–H_2O at 100°: area below ab = Na_2SO_4 field; area abc = solid solution of Na_2SO_4 and Na_2CO_3; area above bc = $Na_2CO_3 \cdot H_2O$ field; O, points fixing equilibria.

Figure 5. Solubility Diagram for Na_2CO_3-Na_2SO_4-NaOH-H_2O from Green and Frattali (9)

The triangular diagram (Fig. 5) can be divided into regions according to the nature of the solid phase in equilibrium with the saturated solution. The area above and to the left of univariant line "A" represents solutions in equilibrium with solid $Na_2CO_3 \cdot H_2O$. The area below univariant line "B" represents solutions in equilibrium with anhydrous Na_2SO_4. The area between the two univariant lines represents solutions in equilibria with a solid solution of Na_2CO_3 and Na_2SO_4 ranging in composition from 1.4 $Na_2SO_4 \cdot Na_2CO_3$ to 2.2 $Na_2SO_4 \cdot Na_2CO_3$. The univariant lines in Fig. 5 are directly analogous to

the invariant points in Fig. 3. They represent solutions in equilibrium with two distinct solid phases. These are $Na_2CO_3 \cdot H_2O$ and 1.4 $Na_2SO_4 \cdot Na_2CO_3$ along univariant line "A" and Na_2SO_4 and 2.2 $Na_2SO_4 \cdot Na_2CO_3$ along univariant line "B." These univariant lines have the same significance as the invariant points in the simpler system. A saturated solution with a composition not on the univariant lines will move toward the univariant lines as precipitation proceeds, and once it reaches a univariant line, it will remain on the line while moving toward higher and higher NaOH levels.

The actual solubilities in this system are given by the tie lines which are lines of constant total dissolved solids concentration. This is the manner in which the fourth component, H_2O, is brought into the picture. This may be visualized by considering the solubility diagram as three-dimensional with the lines of constant dissolved solids corresponding to lines of equal elevation. The weight fraction of total dissolved solids does not vary too greatly (from 26 to 30%) over a very wide range of compositions between the two univariant lines. This also tends to be true outside the univariant lines. Thus, as a first approximation, caustic tends to displace Na_2CO_3 and Na_2SO_4 from solution on a weight equivalent basis. Actually, NaOH drives Na_2CO_3 and Na_2SO_4 from solution more rapidly than on a weight-for-weight basis at low NaOH concentrations. It can be seen that the total dissolved solids concentration tends to drop as the proportion of NaOH increases for NaOH concentrations less than about 50% of the dissolved solids. Above this point, the total dissolved solids begins to rise slowly, reflecting the fact that NaOH is very soluble in water. When the solutions are practically depleted in Na_2CO_3 and Na_2SO_4, the total concentration will increase greatly.

Green and Frattali state that the relation between the composition of the solid phase and the proportions of Na_2CO_3 and Na_2SO_4 in the saturated solution for the four-component system is essentially the same as for the simpler Na_2CO_3-Na_2SO_4-H_2O system, shown earlier in Fig. 4. However, this is not quite true. This may be seen by considering the data presented in Table III which is derived directly from their data on univariant lines A and B (see Table II). The proportion of Na_2CO_3 relative to Na_2SO_4 for univariant line A is practically constant at 90% Na_2CO_3 regardless of the amount of NaOH present. Thus, this line agrees with the C-S-W system phase distribution relations. This is not the case with univariant line B. It can be seen that the carbonate content begins at about 13%, dips slightly at lower NaOH concentrations, and then increases strongly at the higher NaOH concentrations. Thus, there is a deviation from the behavior of the simpler C-S-W system. The exact nature of the phase distributions of Na_2CO_3 and Na_2SO_4 for the C-S-H-W system is not defined, since Green and Frattali did not measure the solid phase compositions in sufficient detail to identify them. However, if the bound of the solid solution remained at 2.2 $Na_2SO_4 \cdot Na_2CO_3$ in this case, the phase distributions would be as shown in Fig. 6. Since Na_2CO_3 and Na_2SO_4 are the substances which do precipitate, the amounts of these two substances which are dissolved (rather than total dissolved solids as in Fig. 5) is of major interest. Solution concentrations of Na_2CO_3 + Na_2SO_4 for the two univariant lines are plotted in Fig. 7 versus NaOH concentration. Concentrations of Na_2CO_3 and Na_2SO_4 in the intermediate region between univariant lines "A" and "B" may be estimated by interpolating according to the fraction of Na_2CO_3 present. It is of interest to note that line B shows a rather sudden change in shape to cross line A and that this appears to correlate with the deviations also noted with the phase distribution behavior.

TABLE III

SOLUBILITY DATA FOR Na_2CO_3-Na_2SO_4-NaOH-H_2O SYSTEM

Univariant Line A			Univariant Line B		
g Na_2CO_3+Na_2SO_4 / 100 g H_2O	g NaOH / 100 g H_2O	$\frac{Na_2CO_3}{Na_2CO_3+Na_2SO_4}$, %	g Na_2CO_3+Na_2SO_4 / 100 g H_2O	g NaOH / 100 g H_2O	$\frac{Na_2CO_3}{Na_2CO_3+Na_2SO_4}$, %
46.5	0	90.0	44.1	0	13.1
45.8	1.3	90.1	39.5	2.1	12.2
43.0	3.7	90.1	34.5	4.7	12.1
40.8	3.8	90.1	34.5	4.6	11.7
37.1	6.0	90.0	30.2	7.0	10.9
37.7	5.4	90.5	26.6	9.5	11.3
33.6	7.6	90.4	19.2	16.0	17.6
27.5	12.0	90.4	13.0	22.0	21.9
27.0	12.1	89.8	9.8	29.9	32.9
21.7	16.6	89.3	5.0	45.8	39.4
16.5	21.2	90.0			
12.2	26.2	90.9			
7.9	32.6	89.4			
5.3	38.8	86.6			

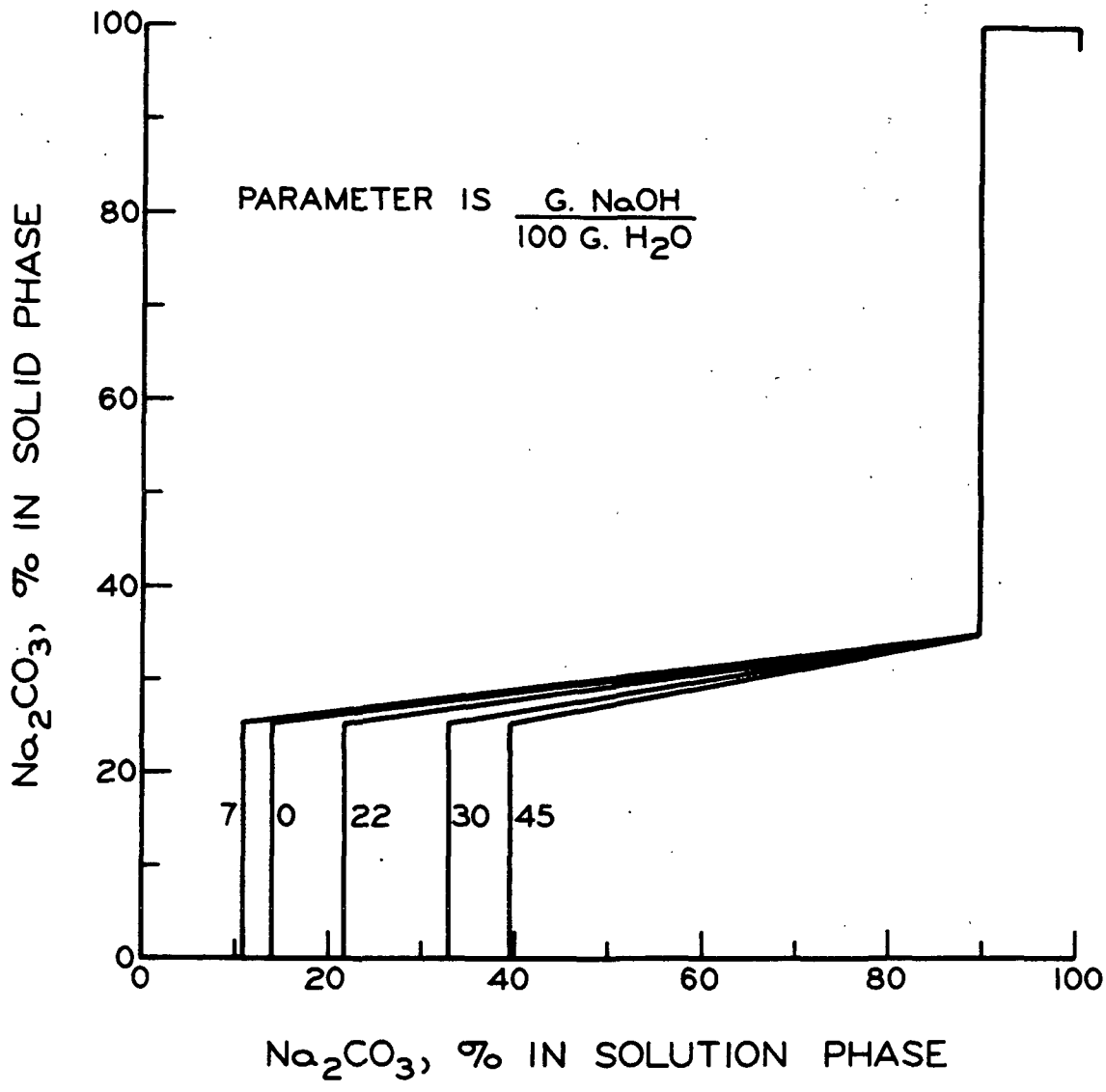


Figure 6. Phase Distribution Data for Na_2CO_3-Na_2SO_4-NaOH-H_2O

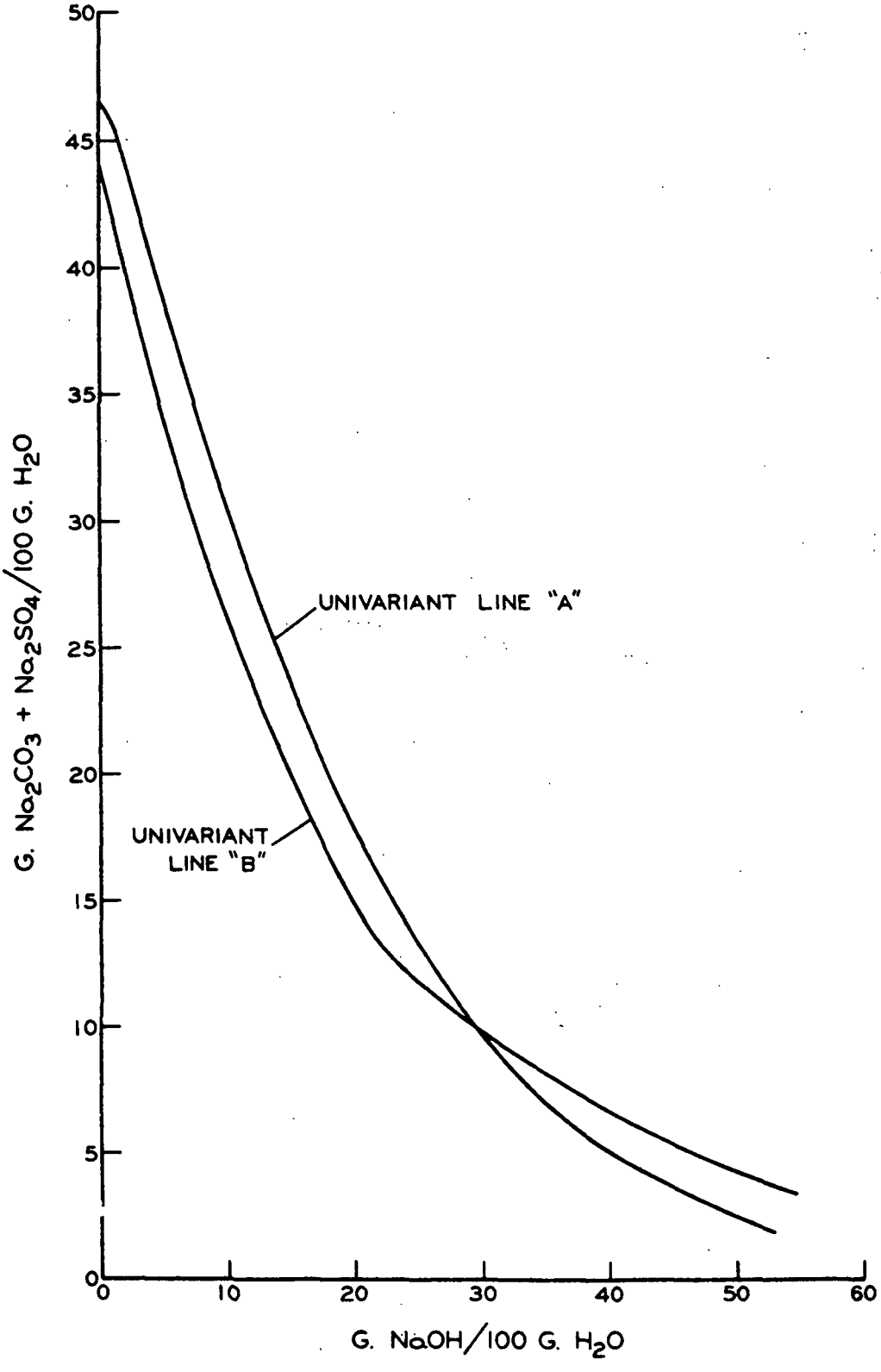


Figure 7. Solubilities of Na_2CO_3 and Na_2SO_4 in Caustic Solutions

Application to Black Liquor

Since black liquor is a fairly strong alkaline solution containing some Na_2CO_3 and Na_2SO_4, it is logical to try to interpret the solubility data in black liquor in terms of the findings of Green and Frattali on the inorganic C-S-H-W system. There are several factors involved in such an analysis. The first is to identify the specific components in the black liquor which play the role corresponding to NaOH in the C-S-H-W system. Diedrichs and Hedstrom (6) have suggested that this is all of the sodium salts in the liquor other than Na_2CO_3 and Na_2SO_4, although they did not test this hypothesis experimentally. Their assumption is a logical starting point. The second question is with regard to the organics. This involves possible competition for water with the inorganics, formation of solubilizing complexes, and possible effects on the phase distribution behavior.

CARBONATE-SULFATE SOLUBILITY IN BLACK LIQUOR

The majority of the experiments in this program were directed toward the study of the solubilities of Na_2CO_3 and Na_2SO_4 in black liquor. Preliminary runs were carried out in Experiment 3 in which the liquors were concentrated to high solids contents and the composition of the precipitated solids determined. These data showed that Na_2CO_3 and Na_2SO_4 were the major components of the solid phase for all eight liquors tested in Experiment 3. An extensive study of the Na_2CO_3/Na_2SO_4 solubility then ensued. The experiments which have a direct bearing on this problem are Experiments 3, 4, 5, 6, 7, 8, 9, 12, 13, and 15. Descriptions of these experiments and summaries of the solubility data obtained are given in Appendix II.

Basic Behavior

A comprehensive set of Na_2CO_3-Na_2SO_4 solubility data on eight different black liquors at a total liquor solids content of about 45% was obtained in Experiment 4. Solubilities were determined at three levels of Na_2CO_3-Na_2SO_4 addition for each liquor. This set of data was considered to define the basic solubility behavior of carbonate and sulfate in black liquor. Comparison with the known inorganic C-S-H-W system was based on two aspects:

1. The relationship between the relative amounts of Na_2CO_3 and Na_2SO_4 existing in the solution phase and that in the solid phase. (This is referred to as phase distribution data.)
2. The actual amounts of Na_2CO_3 and Na_2SO_4 which are soluble in the black liquor. (These are referred to as saturation concentrations.)

According to the data of Green and Frattali on the C-S-H-W system, the relative proportions of Na_2CO_3 and Na_2SO_4 in solution are determined solely by the composition of the solid phase. This hypothesis can be easily tested with the black liquor data. The amount of soluble carbonate is divided by the sum of carbonate + sulfate and expressed as % Na_2CO_3 in the solution phase. A similar procedure is carried out on the solid phase data. These phase distribution data may then be compared to the Green and Frattali prediction. In examining these phase distribution data, it must be borne in mind that they are concerned only with Na_2CO_3 and Na_2SO_4. All other liquor components are ignored.

The saturation concentrations are best compared on the basis of the sum of Na_2CO_3 and Na_2SO_4 dissolved in the liquor. This is done because the

relative proportions of carbonate and sulfate should be set by the phase distribution relationships, and because the combined saturation concentrations are not strongly dependent on the relative amounts present (see Fig. 7).

In analyzing the saturation data in black liquors, the assumption of Diedrichs and Hedstrom is made. The black liquor is assumed to act like a solution of Na_2CO_3, Na_2SO_4 and other sodium salts, and these other sodium salts are assumed to affect the solubility of Na_2CO_3 and Na_2SO_4 as if they were NaOH. In this manner, the very complex black liquor system may be reduced to a four-component system containing Na_2CO_3, Na_2SO_4, "NaOH" and H_2O. The equivalent "NaOH" is found by taking the total sodium content of the black liquor, subtracting the sodium present as Na_2CO_3 and Na_2SO_4 in the black liquor, and then multiplying by 40/23. The water present expressed as % on the liquor solids is found by $100 \times \left(\frac{100 - \%\text{ liquor solids}}{\%\text{ liquor solids}}\right)$.

The amount of Na_2CO_3 and Na_2SO_4 dissolved in the liquor (based on the Na_2CO_3-Na_2SO_4-"NaOH"-H_2O analogy) may be calculated from either the triangular diagram (Fig. 5) or from Fig. 7. It appears that Fig. 7 may be slightly more convenient to use even though it is necessary to interpolate between the two lines based on the relative amounts of carbonate and sulfate in solution. The analysis of the data from Experiment 4 was based on Fig. 5 because it was felt to involve less interpolation error. The percentages of Na_2CO_3, Na_2SO_4 and "NaOH" were calculated to give the coordinates for Fig. 5. The % d.s. (dissolved solids) in solution was then read from the figure. The predicted amounts of $Na_2CO_3 + Na_2SO_4$ based on liquor solids were calculated by taking

$$\frac{(\%\ Na_2CO_3 + \%\ Na_2SO_4)}{(\%\ Na_2CO_3 + \%\ Na_2SO_4 + \%\ NaOH)} \times \frac{\%\text{ d.s.}}{(100 - \%\text{ d.s.})} \times \text{water (\% on liquor solids)}.$$

A summary of the results of analyzing the data from Experiment 4 is given in Table IV. This includes a comparison between the measured amounts of soluble Na_2CO_3 and Na_2SO_4 and that predicted by the equivalent "NaOH" approach. The phase distribution data are also presented. These latter data are plotted in Fig. 8 in which the expected curve (based on the C-S-W system) is also shown.

It can be seen that there is quite good agreement between the amounts of Na_2CO_3 and Na_2SO_4 actually found in the solution phase, and that expected from the analogy with the C-S-H-W system. There is agreement in both magnitude and trend. It appears that liquor composition variables (other than sodium content) may have a slight effect on the solubility, since the measured values are somewhat lower than predicted for Liquors B and E. However, the differences are quite small and these variables do not appear to have major significance. The major liquor compositional variable affecting Na_2CO_3 and Na_2SO_4 solubility is the total sodium content. The various sodium compounds in the liquor can be treated as if they were NaOH as far as the solubilities of carbonate and sulfate are concerned. It is clear that the data of Green and Frattali for the C-S-H-W system are applicable to the prediction of solubilities in black liquor (at least at 45% solids).

The phase distribution data also agree quite well with the distributions given by Green and Frattali for the simpler systems. With the exception of a few points where the amount of Na_2CO_3 in the solid phase is lower than expected (4-A-2, 4-A-3, 4-G-1, and 4-G-2), the data fit the line corresponding to the solid solution region. The reasons for deviations are not clear. In the case of Liquor A, there was a fairly substantial organic content in the solid phase (fiber, soap, and hydrocarbon oils) which might have influenced the distribution data. However, the organic content of the solid phase was

TABLE IV

ANALYSIS OF SOLUBILITY DATA FROM EXPERIMENT 4

Sample	Liquor Solids	"NaOH," % on solids	Measured $Na_2CO_3+Na_2SO_4$	Predicted $Na_2CO_3+Na_2SO_4$	Na_2CO_3 Solution, %	Na_2CO_3 Solid, %
4-A-1	47.9	21.1	20.2	18.9	59	29
4-A-2	47.0	19.7	19.1	19.6	48	17
4-A-3	46.6	21.3	18.3	18.4	45	12
4-B-1	46.1	23.1	18.9	19.2	68	38
4-B-2	46.0	23.2	16.1	17.3	65	28
4-B-3	45.7	23.4	13.6	15.8	51	24
4-C-1	46.3	21.7	18.5	18.9	56	33
4-C-2	45.7	21.6	15.6	17.3	47	29
4-C-3	45.2	22.3	15.6	16.9	37	27
4-D-1	47.3	18.7	22.5	21.8	66	32
4-D-2	47.3	19.8	21.4	20.6	59	33
4-D-3	46.5	20.9	18.8	19.2	50	29
4-E-1	47.1	21.6	19.7	19.1	65	34
4-E-2	46.2	22.8	16.8	17.6	60	27
4-E-3	45.2	23.2	14.9	17.0	50	26
4-F-1	48.1	21.1	20.2	18.9	65	34
4-F-2	46.5	22.8	16.3	17.2	52	31
4-F-3	46.1	21.9	15.8	17.2	45	28
4-G-1	47.5	21.5	21.9	19.9	61	23
4-G-2	47.3	21.3	19.4	18.9	54	21
4-G-3	46.7	21.5	17.2	17.7	47	25
4-H-1	47.7	21.5	22.3	20.0	65	38
4-H-2	46.4	21.3	20.3	20.0	57	31
4-H-3	45.8	22.8	18.0	18.3	49	30

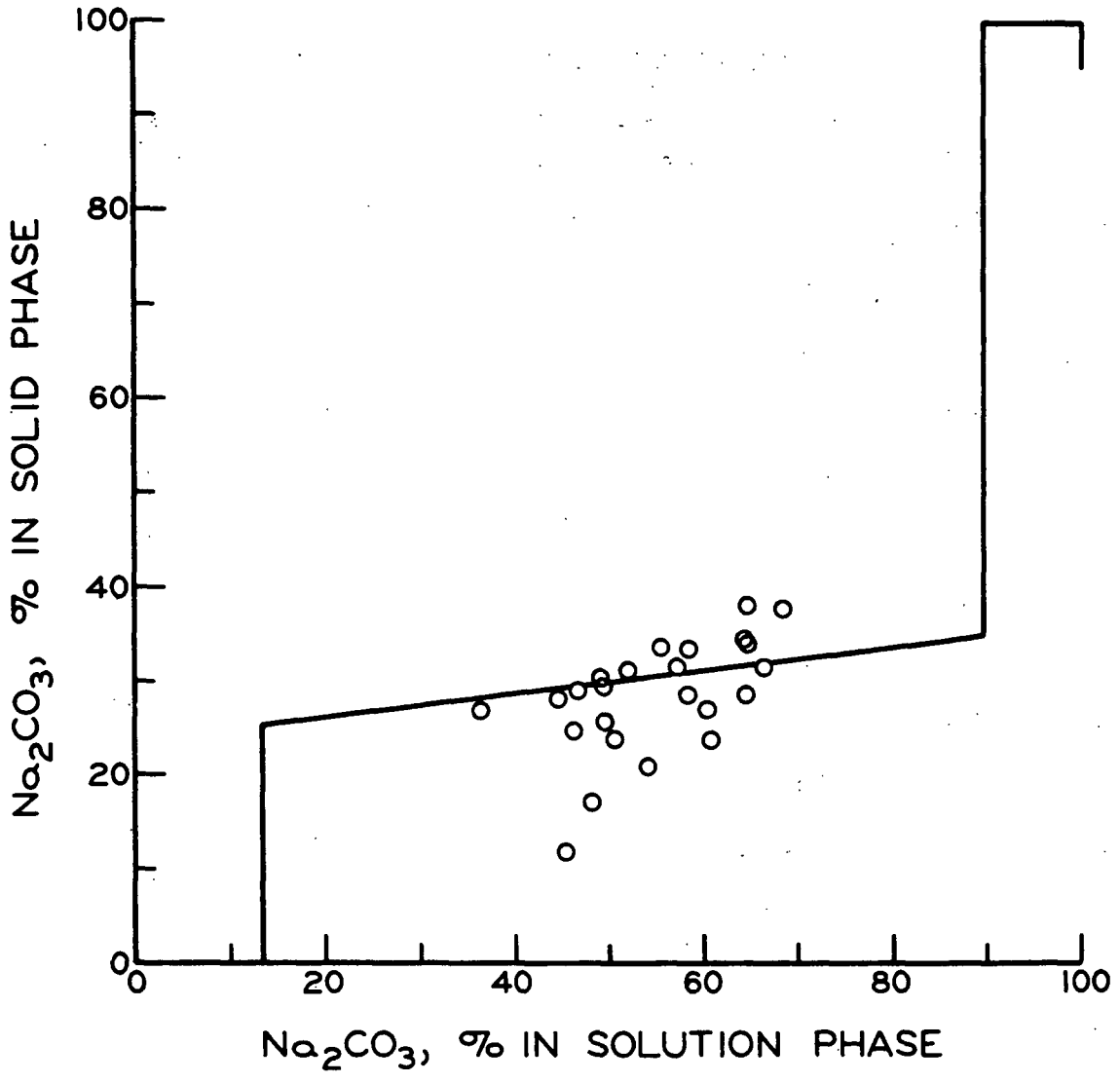


Figure 8. Phase Distribution Data for Experiment 4

nearly zero for the G runs, so this cannot be the whole answer. It is possible that the deviations reflect mainly experimental inaccuracies with the solid phase samples.

In general, the results of Experiment 4 could be readily interpreted in terms of the known solubility behavior of the C-S-H-W system. The agreement of the phase distribution data for the liquor with that for the purely inorganic system indicated that the same solid phase compounds were involved in both cases. The agreement of saturation concentrations with predictions substantiates the equivalent "NaOH" hypothesis of Diedrichs and Hedstrom and appears to indicate all of the water in the liquor is available for solubilizing carbonate and sulfate.

The variable coverage in Experiment 4 is somewhat limited. In particular, the liquor solids was held at about 45% solids, and it might be expected that agreement with the C-S-H-W system would be better at low solids contents. In addition, the relative amounts of Na_2CO_3 and Na_2SO_4 within the system in Experiment 4 were such as to force the solid phase into the solid solution. The proportion of sulfate was greater than it might be in most liquors and this is another limitation.

Effect of Liquor Solids Content

Several experiments were directed toward the effect of total liquor dissolved solids content on Na_2CO_3-Na_2SO_4 solubility. The experiments involving different solids contents at 100°C were Experiments 3, 5, and 13. Experiment 12 also has bearing on the problem since it was carried out at about 65% solids; however, it was done at 120°C and this involves another variable.

The major effect of an increase in liquor solids content is a decrease in the ratio of water to liquor solids. This can become very significant above

50% solids (e.g., increasing liquor solids content from 50 to 65% will cut the water to solids ratio nearly in half). If the amount of soluble carbonate and sulfate is proportional to the amount of water present, their solubility will be rapidly decreased in high solids black liquor. Because of the sensitivity of the water to solids ratio at high liquor solids contents, these solubility determinations are strongly influenced by the accuracy of the solids content measurement. Another effect of high liquor solids contents is a greater proportion of organics in the solution phase. Thus, any influence of the organic constituents on carbonate-sulfate solubility should be enhanced in high solids content black liquor.

The approach taken in examining the effect of liquor solids content was to reduce the data to an equivalent Na_2CO_3-Na_2SO_4-"NaOH"-H_2O system and compare the results to Green and Frattali's data. This had been shown to be generally applicable to 45% solids data, so that any deviations from the predicted results could be interpreted as being due to the change in solids content. A summary of the results of analyzing the data from Experiments 3, 5, and 13 in terms of the equivalent "NaOH" analogy is given in Table V. The procedure for carrying out the data reduction was identical to that described earlier for Experiment 4.

Examination of the data in Table V indicates that the liquor solids content does affect the solubility of Na_2CO_3 and Na_2SO_4 above and beyond the simple effect on the water to solids ratio. Changes occur in both the saturation and phase distribution behavior. In general, the solubility of Na_2CO_3 + Na_2SO_4 is greater than expected at high liquor solids contents. This may be seen in Fig. 9, in which the percentage deviation from the predicted solubility is plotted <u>versus</u> the liquor solids content. Although there is a good deal of scatter,

TABLE V

ANALYSIS OF SOLUBILITY DATA FROM EXPERIMENTS 3, 5, AND 13

Sample	Liquor Solids	"NaOH," % on solids	Measured $Na_2CO_3+Na_2SO_4$, % on solids	Predicted $Na_2CO_3+Na_2SO_4$, % on solids	Na_2CO_3 Solution, %	Na_2CO_3 Solid, %
3-A-1	63.6	25.4	6.2	4.75	61	93
3-B-1	69.7	25.3	7.2	3.9	81	85
3-C-1	57.9	22.6	7.2	6.95	64	38
3-D-1	62.6	23.8	6.0	4.95	72	77
3-E-1	64.7	24.9	5.4	4.1	72	76
3-F-1	58.1	21.1	10.5	9.1	74	49
3-G-1	64.8	26.7	3.7	3.0	60	64
3-H-1	58.7	15.8	12.8	11.7	87	77
5-A-1	43.4	18.2	28.5	28.1	58	23
5-A-2	47.1	22.4	20.9	19.4	64	35
5-A-3	50.2	22.9	17.3	15.6	69	34
5-A-4	55.2	23.2	13.7	11.3	74	36
5-A-5	59.2	25.0	10.6	7.8	76	40
5-C-1	42.8	19.9	25.7	26.9	55	31
5-C-2	45.5	23.0	20.4	20.5	60	34
5-C-3	49.6	23.4	15.6	15.1	64	39
5-C-4	53.4	24.1	12.8	11.4	65	43
5-C-5	59.6	--	--	--	--	46
13-A-1	59.1	27.9	9.4	6.95	78	75
13-C-1	54.8	27.8	10.6	8.85	75	60
13-D-1	57.7	26.5	8.9	7.4	81	74
13-G-1	57.6	28.2	8.3	6.8	68	66
13-H-1	58.4	28.5	8.8	6.8	81	74

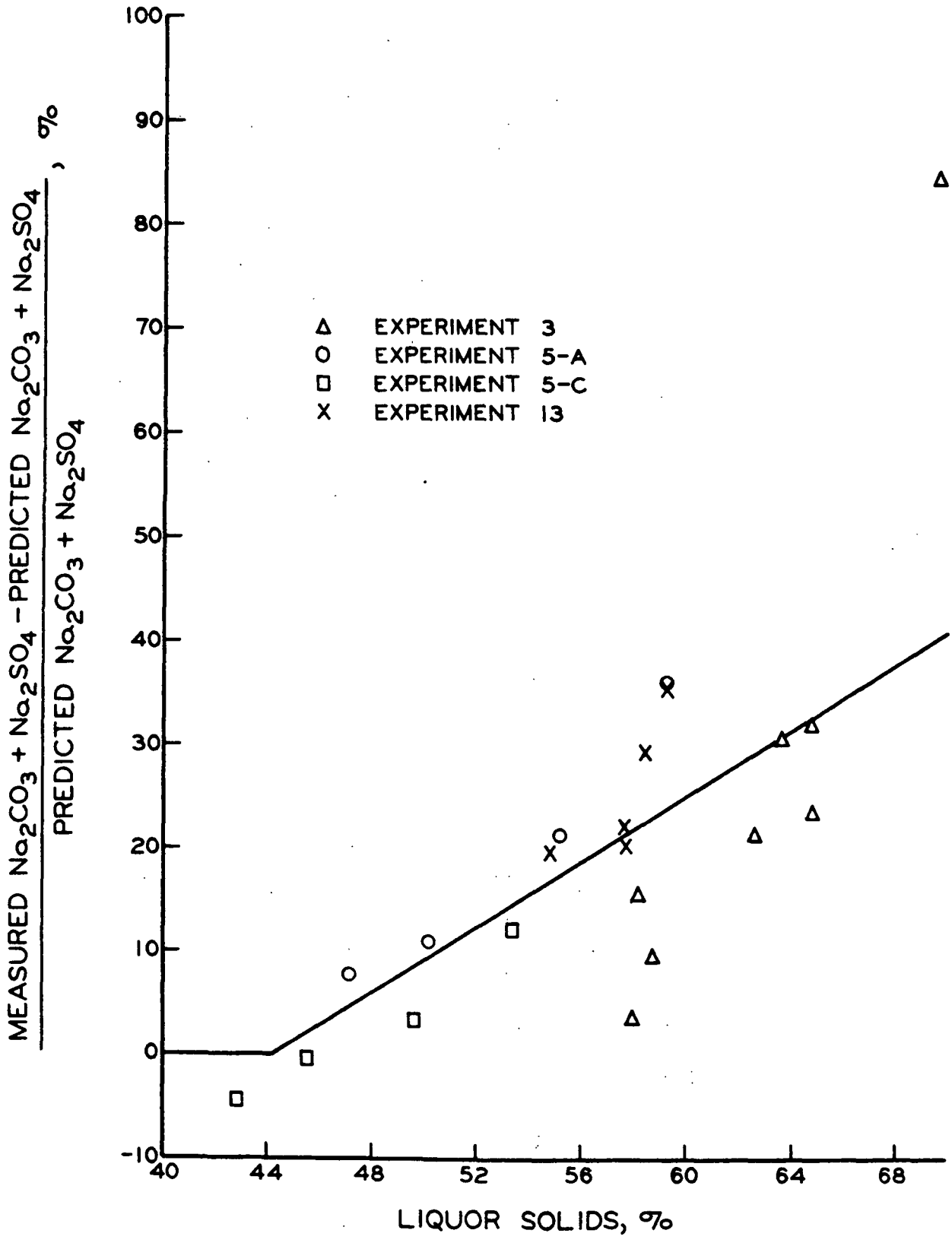


Figure 9. Effect of Liquor Solids Content on Solubility of Na_2CO_3 and Na_2SO_4

there is a clear trend of increasing deviation with increasing liquor solids content. This is definitely seen in Experiment 5, in which liquor solids content was the major variable. There were some minor differences between the two liquors used in Experiment 5, although the rate of increase in the deviation with respect to increasing solids content is quite similar. The straight line shown on Fig. 9 was drawn between the data for Liquor A and Liquor C. Material balances (presented in Appendix III) indicate that it is questionable whether or not saturation conditions really existed in the lowest solids runs in Experiment 5. This is especially true for Liquor A. The solution sample for the highest solids run in 5-C was lost before the Na_2SO_4 content could be measured, and, thus, that sequence was not completed. The data from Experiment 13 agree quite well with the results from Experiment 5. The results from Experiment 3 are somewhat lower (with the exception of 3-B-1). The reason for this is not known, but Experiment 3 was carried out early in the program and the data may not be the most reliable.

The phase distribution data for Experiments 3, 5, and 13 are shown in Fig. 10. All of these data show the solid phase to be richer in Na_2CO_3 and the solution phase richer in Na_2SO_4 than expected. The deviations appear to increase with increasing liquor solids content. This may be seen by considering the points for the two liquors of Experiment 5. Experiment 5 was carried out with the addition of relatively large amounts of Na_2CO_3 and Na_2SO_4 to the liquors, which would tend to force the solid phase into the 1.4-2.2 $Na_2SO_4 \cdot Na_2CO_3$ solid solution region. The deviations from this line are not too great. Much greater deviations are found in those experiments in which the Na_2CO_3 and Na_2SO_4 originate entirely with the liquor. In these cases, the entire systems tend to be richer in carbonate, and there is a more severe test of the phase distribution predictions.

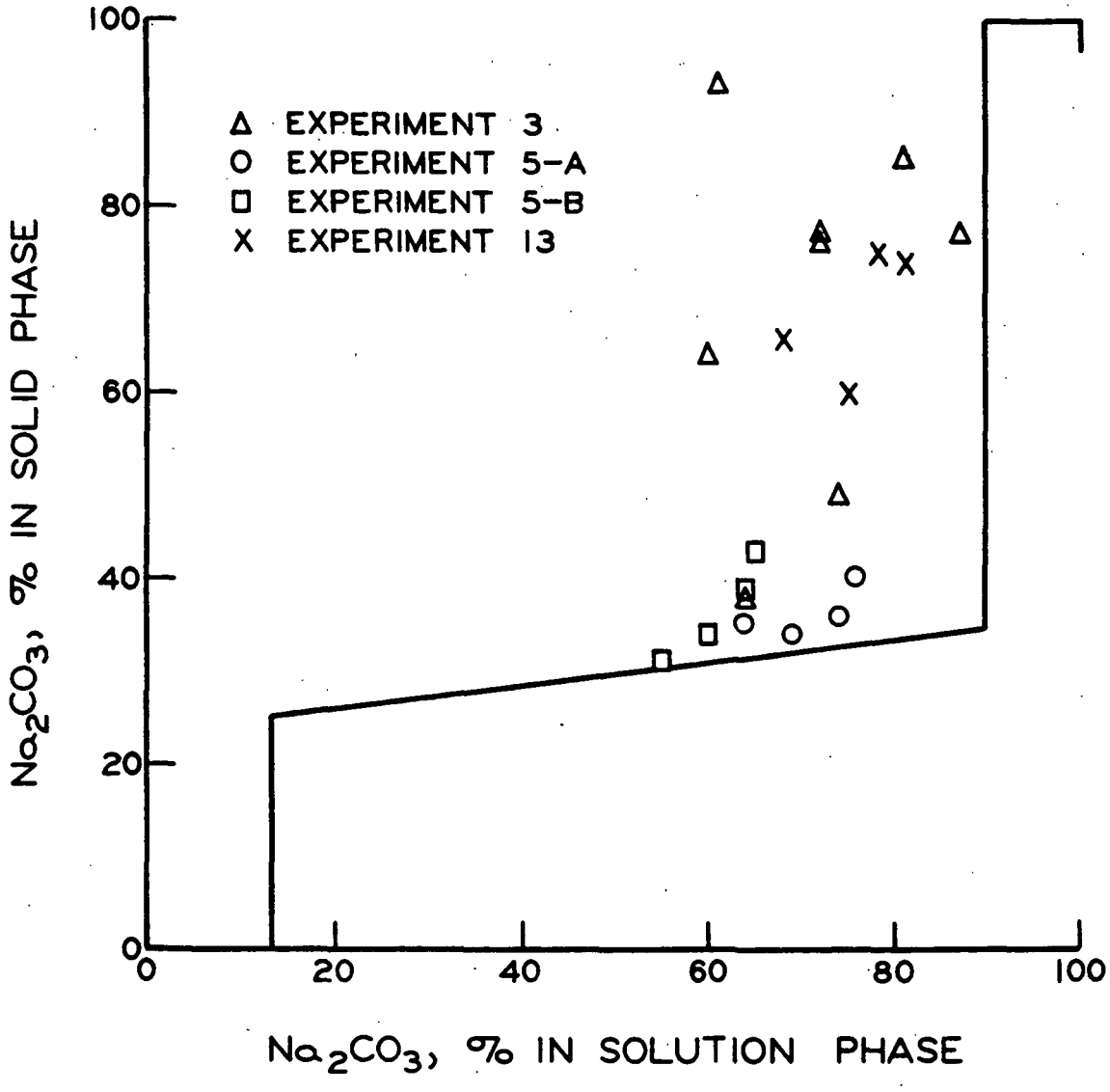


Figure 10. Phase Distribution Data for Experiments 3, 5, and 13

Considering the material balances as well as the measured data, it is clear that the deviations in the phase distribution data are due to the Na_2SO_4 being more soluble than expected in high solids black liquor, and not to errors in the measured composition of the solid phase. According to Green and Frattali, the key solution phase proportion in a carbonate rich system is 90% Na_2CO_3 and 10% Na_2SO_4. If the proportion of Na_2CO_3 in the solution is less than 90%, a relatively sulfate rich (> 1.4 $Na_2SO_4 \cdot Na_2CO_3$) solid solution will precipitate while the solution will move toward the 90% Na_2CO_3 condition. The proportion of Na_2CO_3 in the solid phase should not rise above about 35% until the solution is 90% Na_2CO_3. This is not what is found with the high solids black liquors, where the solid phase is rich in Na_2CO_3 even though the solution phase contains only 60 to 80% Na_2CO_3.

The "expected" phase distribution behavior can be made clearer by considering how the composition of the solution and solid phase would vary as a function of extent of precipitation for any given starting composition. Since a unique relation exists between the composition of the solution and solid phases (see Fig. 3), it is possible to construct diagrams showing how the phase distributions should change with extent of precipitation. These are given in Fig. 11 and 12 for the solution and solid phases, respectively. It is clear that the solution composition moves to the univariant points and the solid phase is normally sulfate rich.

The material balance data given in Appendix III can be used to determine the extent of deviation from the expected phase distribution behavior. These data are used to calculate the carbonate proportion (% Na_2CO_3) for the entire system (from the input data) and the extent of precipitation of Na_2CO_3

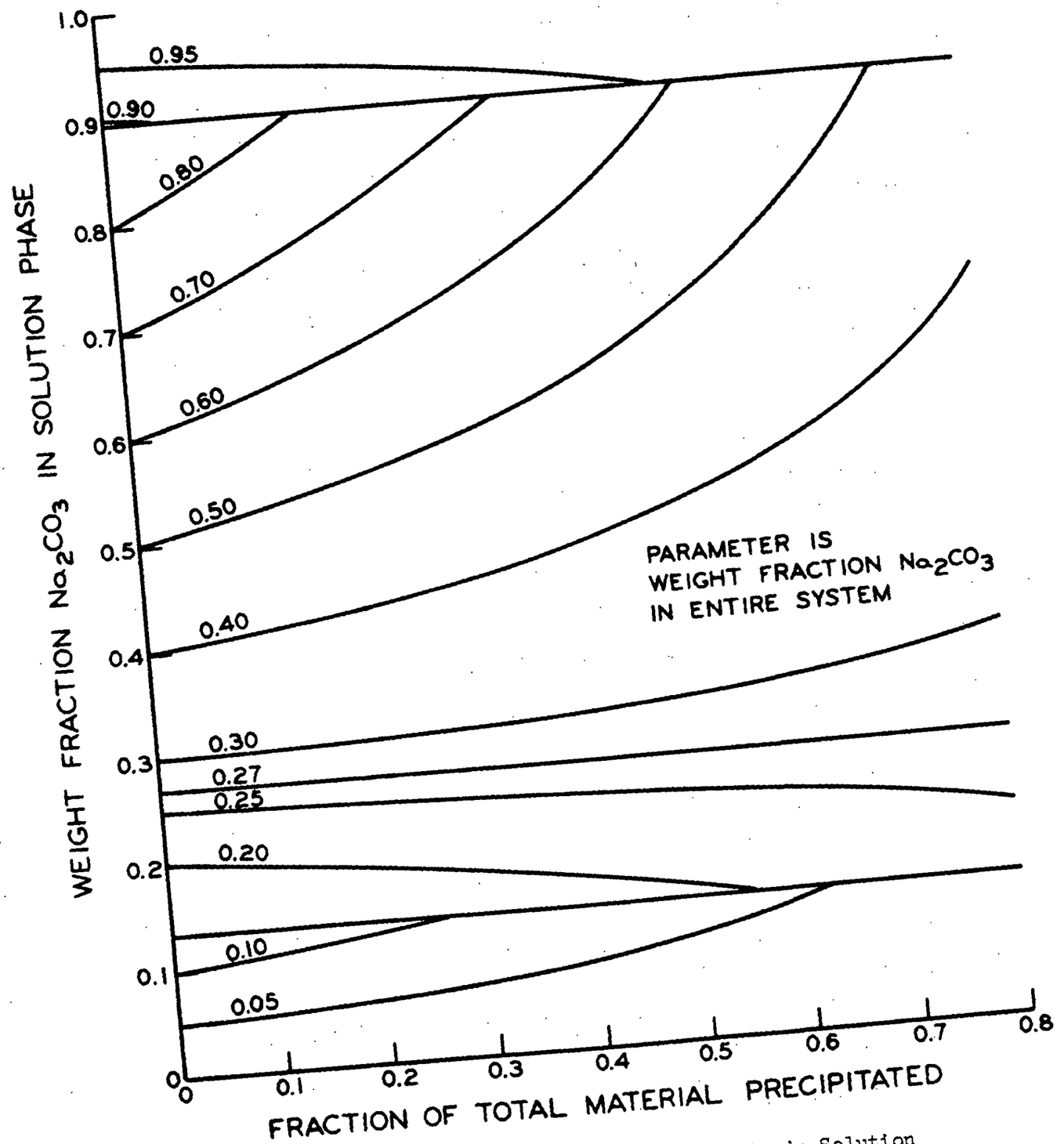


Figure 11. "Expected" Proportion of Carbonate in Solution Phase *vs.* Extent of Precipitation

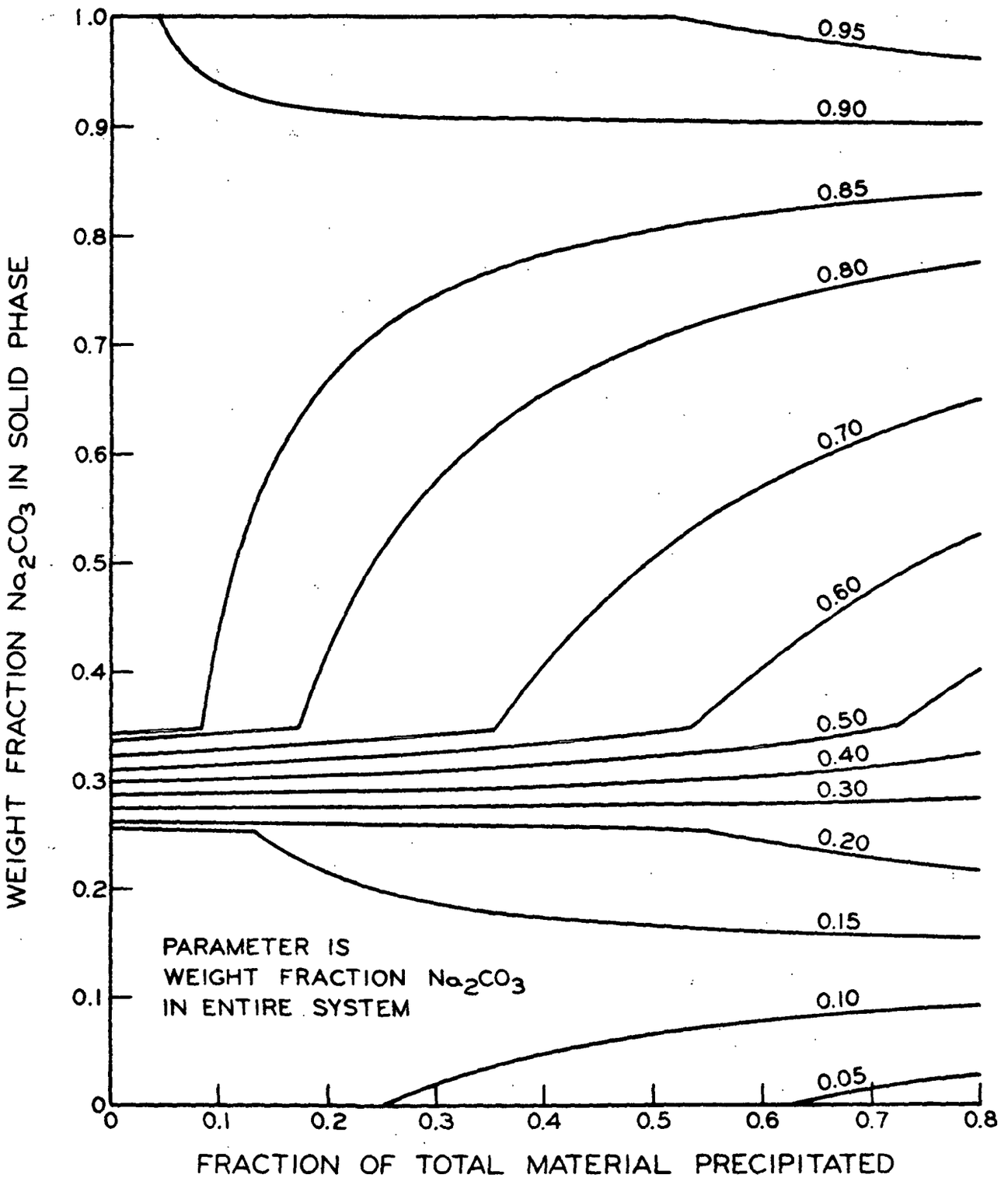


Figure 12. "Expected" Proportion of Carbonate in Solid Phase vs. Extent of Precipitation

and Na_2SO_4. Figure 11 is then used to determine the "expected" carbonate proportion in the solution phase. This value may then be used to calculate the expected Na_2SO_4 concentration (% on solids) in the solution phase from the measured Na_2CO_3 concentration. The results of this analysis are shown in Table VI. It can be seen that the lower solids content data, and those for which the expected solution concentration is not on the invariant line, fit the prediction within the accuracy of the data. Those data which are expected to be on the invariant line deviate significantly. The % Na_2SO_4 tends to be about 1-2% higher (based on solids) than expected. This may mean that some of the Na_2SO_4 tends to associate with the dissolved organics at the high solids levels. It may also reflect a tendency for the organics in black liquor to shift the carbonate-rich invariant line to lower carbonate proportions.

Effect of Temperature

Most of the experiments were carried out at a temperature of 100°C. Three experiments were carried out at higher temperatures in order to gain some understanding of temperature effects. Experiments 8 and 9 were done at 120 and 140°C, respectively, with relatively low solids liquors (about 45%). Experiment 12 was carried out at 120°C and a solids content of about 65%. A summary of saturation and phase distribution data for these three experiments is given in Table VII.

There is generally good agreement between the measured and predicted saturation concentrations for Experiment 8. This is basically what was found with Experiment 4, and indicates that there is little change in the solubilities between 100 and 120°C. In Experiment 9, on the other hand, the measured concentrations are slightly lower than predicted. Comparing each run in Experiment 9 with the corresponding run in Experiment 8, shows that there is about a 10% reduction in the solubility of Na_2CO_3 + Na_2SO_4 in going from 120 to 140°C.

TABLE VI

ANALYSIS OF PHASE DISTRIBUTIONS DATA FROM EXPERIMENTS 3, 5, AND 13

Sample	Na_2CO_3 System, %	Extent of Pptn., %	Expected % Na_2CO_3 Solution	Predicted Na_2SO_4, % on solids	Measured Na_2SO_4, % on solids	Liquor Solids
3-A-1	81.6	38.0	90	0.42	2.4	63.6
3-B-1	85.1	36.7	90	0.65	1.4	69.7
3-C-1	55.4	25.5	63.5	2.64	2.6	57.9
3-D-1	81.4	61.5	90	0.48	1.7	62.6
3-E-1	80.3	53.3	90	0.43	1.5	64.7
3-F-1	65.9	14.6	71.5	3.11	2.7	58.1
3-G-1	72.6	68.5	90	0.25	1.5	64.8
3-H-1	Material balance invalid					58.7
5-A-1	Saturation condition doubtful					43.4
5-A-2	61.4	7.2	63.5	7.7	7.5	47.1
5-A-3	63.6	10.8	68	5.65	5.3	50.2
5-A-4	67.0	16.4	73.5	3.65	3.6	55.2
5-A-5	67.5	35.8	86.5	1.25	2.6	59.2
5-C-1	53.3	6.8	56	11.1	11.6	42.8
5-C-2	53.9	16.0	58.5	8.7	8.1	45.5
5-C-3	54.7	26.8	63	5.9	5.6	49.6
5-C-4	55.6	29.1	65	4.4	4.6	53.4
5-C-5	Solution analysis incomplete					59.6
13-A-1	Material balance invalid					59.1
13-C-1	70.3	49.3	90	0.88	2.7	54.8
13-D-1	76.0	43.2	90	0.80	1.7	57.7
13-G-1	76.7	50.4	90	0.62	2.7	57.6
13-H-1	75.9	27.8	90	0.79	1.7	58.4

TABLE VII

ANALYSIS OF SOLUBILITY DATA FROM EXPERIMENTS 8, 9, AND 12

Sample	Liquor Solids	"NaOH," % on solids	Measured Na_2CO_3 + Na_2SO_4	Predicted Na_2CO_3 + Na_2SO_4	Meas.-Pred. / Pred., %	Na_2CO_3 Solution, %	Na_2CO_3 Solid, %
8-A-1	48.5	21.6	17.5	17.2	1.7	62	36
8-C-1	47.8	23.0	17.9	17.6	1.7	67	35
8-D-1	47.5	20.9	21.1	19.9	6.0	62	39
8-E-1	47.1	23.6	15.4	16.8	-8.3	68	35
8-H-1	48.4	22.5	19.9	17.8	11.8	61	39
9-A-1	43.5	22.9	21.1	22.2	-5.0	76	40
9-C-1	42.1	24.9	22.2	23.2	-4.3	67	39
9-D-1	42.0	22.6	23.7	25.2	-6.0	75	42
9-E-1	41.8	25.3	17.8	21.4	-16.8	72	38
9-H-1	42.4	23.5	22.0	23.6	-6.8	78	43
12-B-1	64.9	27.0	5.6	3.95	36.8	64	48
12-D-1	65.5	21.4	8.4	5.6	50.0	75	78
12-F-1	65.6	24.0	7.4	4.95	49.5	62	68
12-G-1	63.9	28.9	5.6	4.95	13.1	55	73
12-I-1	64.7	24.1	5.9	4.4	34.1	61	86

The measured concentrations are all greater than the predicted in Experiment 12. However, this is felt to be due to the high solids content and not the temperature. The percentage deviations from the predicted saturation concentrations fit with the general pattern shown by other high solids liquors as presented in Fig. 9.

Temperature appears to have little effect on the phase distribution behavior as may be seen in Fig. 13. The points for Experiments 8 and 9 lie slightly above the expected line, but within the region of experimental error. There is no

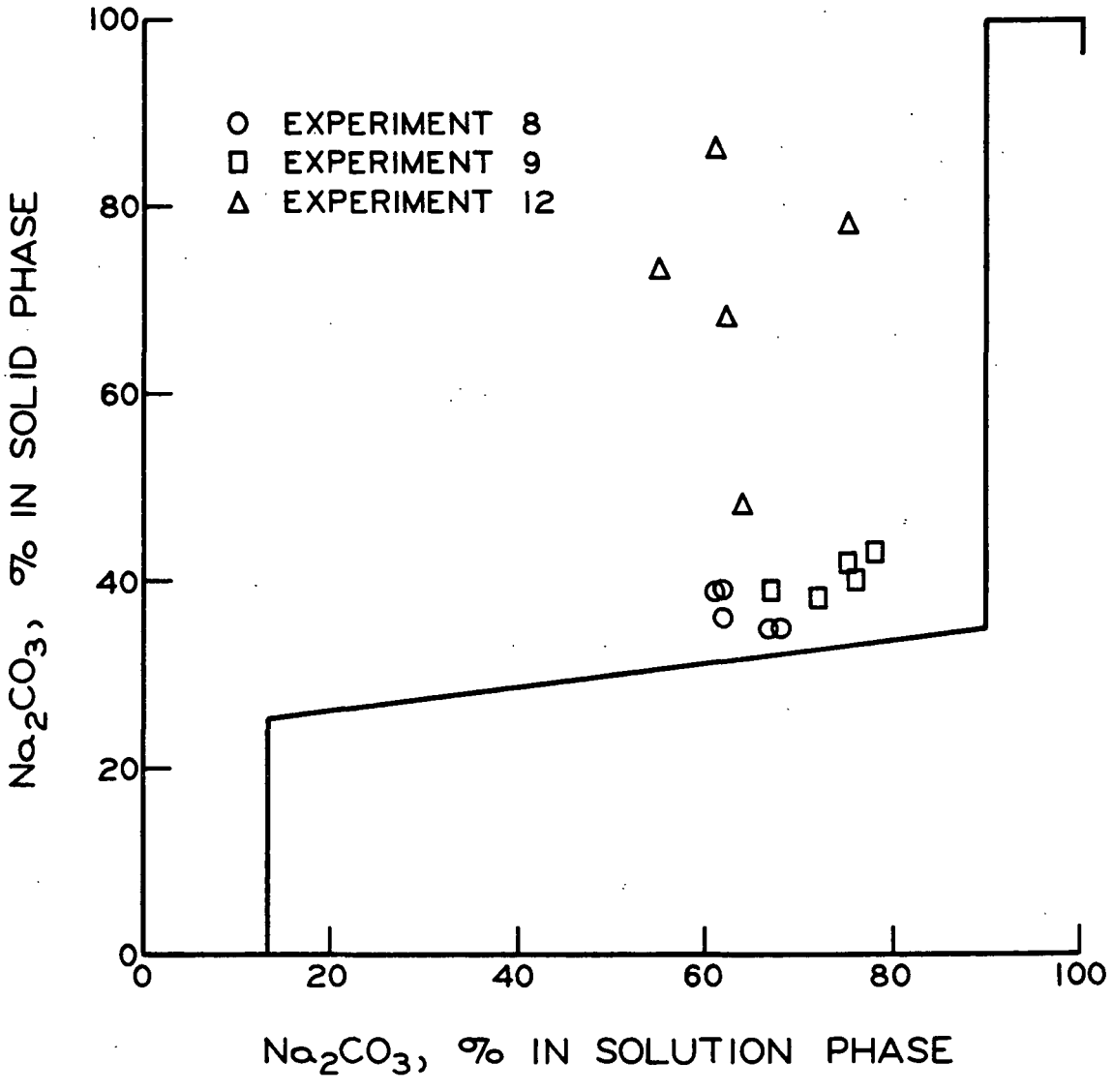


Figure 13. Phase Distribution Data for Experiments 8, 9, and 12

evidence of a change in distribution behavior in going from 120 to 140°C. The points for Experiment 12 show the pattern of higher Na_2SO_4 in the solution phase (and higher Na_2CO_3 in the solid phase) that seems to be typical for high liquor solids runs.

In general, temperature appears to have relatively little effect on the solubility of Na_2CO_3 and Na_2SO_4 in black liquor. The relative proportions of Na_2CO_3 and Na_2SO_4 do not appear to be affected by temperature over the range of 100-140°C. The amounts of Na_2CO_3 and Na_2SO_4 dissolved in the liquor do not appear to be dependent on temperature between 100 and 120°C. There does appear to be a slight reduction of 5 to 10% in the solubility between 120 and 140°C. The fact that temperature does not seem to have a large effect on the solubility behavior may have a bearing on scale formation in evaporators. One of the mechanisms suggested for deposit formation is a decrease in solubility with increasing temperature leading to supersaturation and subsequent precipitation in the hotter regions close to the tube wall. If temperature does not have an appreciable effect on solubility, then it would appear that scaling would have to be due to concentration changes associated directly with the vaporization process itself.

There are some peculiarities in the high temperature data that should be mentioned. Experiments 8 and 9 were designed to be identical in all respects except for the temperature, yet the solids contents for the solution samples from Experiment 9 were all significantly lower than those from Experiment 8. It is believed that this is due to the introduction of additional water into the vessels for Experiment 9 and <u>not</u> because of the exclusion of large quantities of organic by the fritted glass filter at the highest temperature. Extraneous water could enter from either a too dilute Na_2CO_3-Na_2SO_4 solution being added

or from failure to evaporate off all of the water needed. The first attempt to run Experiment 9 ended catastrophically when one of the pressurization lines failed and all of the liquors boiled out violently through the common manifold system. In the confusion caused by cleaning up the mess, changing the experimental system to avoid a similar failure and restarting Experiment 9, too much water could have gotten into the system. The material balances tend to show some deviations in these higher temperature runs. Too much sulfate was found in Experiment 8 and too much carbonate in Experiment 9. Experiment 12 gave reasonably good carbonate-sulfate balances in general, but points 12-B-1 and 12-I-1 have very large material balance deviations. Another general feature of all of the high temperature material balances is that the Na_2O found is less than that introduced into the system. This appears to be due to reactions consuming the strong alkalies at the higher temperature. Deviations in the sulfate-carbonate balances may be due to the method used to obtain solid samples (dissembling the vessels and decanting off the liquor). The solid sample is obtained at a lower temperature than the solution sample, and changes could occur in the time between taking the two samples.

Effect of NaCl

The solubility of NaCl in black liquor and its effect on the solubility of Na_2CO_3 and Na_2SO_4 was examined in Experiment 6. This experiment was carried out on five different liquors at 55% solids and two levels of NaCl addition. Solution samples were taken after each level of NaCl addition, while a solid sample was taken only after the second. The solubility data are given in Appendix II and the relevant material balances in Appendix III.

The data clearly show that NaCl is much more soluble in black liquor than either Na_2CO_3 or Na_2SO_4. It is doubtful if any NaCl is present in the

solid phase after the first level of NaCl addition (about 6% on the solids), and with most of the liquors it appears to be totally soluble at 12% on the solids. Only Liquor C shows definite evidence of a small amount of NaCl precipitation at 12% NaCl on the solids. Liquors D and G show negligible NaCl in the solid phase. The solid samples for Liquors E and F show the presence of significant NaCl, but this is contradicted by the material balances. It appears that NaCl is soluble in liquor to at least 10% on the solids at a total solids content of 55%. This would be equivalent to about 12 g NaCl/100 g H_2O. This is considered to be a lower limit for NaCl solubility in black liquor. Higher values were observed in Experiment 6; for example, with Liquor G the solubility is at least 16 g NaCl/100 g H_2O.

The main effect of NaCl in black liquor is a tendency to repress the solubility of Na_2CO_3 and Na_2SO_4. The NaCl acts in a similar manner to the other sodium salts in the black liquor. This can be seen by calculating the equivalent "NaOH" for the runs in Experiment 6 in the usual manner and comparing predicted solubilities with those measured. A summary of the results of analyzing the data from Experiment 6 is given in Table VIII. The measured values of the Na_2CO_3 + Na_2SO_4 concentration are about 30% greater than those predicted for all of the points. This appears to be related to the solids content at which the experiment was carried out. The deviations given in Table VIII are slightly higher than the line drawn in Fig. 9 but they do seem to be in general alignment with the points from Experiment 13. Thus, NaCl appears to have the same effect on Na_2CO_3 and Na_2SO_4 solubility as NaOH. The phase distribution behavior in Experiment 6 is typical of the data for other high solids experiments.

TABLE VIII

ANALYSIS OF SOLUBILITY DATA FROM EXPERIMENT 6

Sample	Liquor Solids	NaCl, % on solids	"NaOH," % on solids	Measured Na_2CO_3 + Na_2SO_4	Predicted Na_2CO_3 + Na_2SO_4	Meas.- Pred. / Pred.	Na_2CO_3 Solution, %	Na_2CO_3 Solids, %
6-C-1	55.5	6.4	27.1	11.9	9.4	26.6	--	--
6-C-2	56.4	12.4	32.5	8.8	6.65	32.4	77	56
6-D-1	56.7	7.2	26.7	10.8	8.5	27.1	--	--
6-D-2	56.8	12.5	29.3	8.7	7.0	24.3	78	73
6-E-1	58.2	6.8	28.4	10.5	7.6	38.2	--	--
6-E-2	57.5	12.6	31.9	6.1	5.05	20.8	77	69
6-F-1	56.7	6.6	28.5	10.2	7.95	28.3	--	--
6-F-2	57.0	12.1	30.0	9.8	7.4	32.4	65	49
6-G-1	57.7	6.5	27.7	10.7	7.95	34.6	--	--
6-G-2	57.9	12.2	31.8	8.3	6.2	33.9	69	63

Effect of $Na_2S_2O_3$

The solubility of sodium thiosulfate in black liquor and its effect on the solubility of Na_2CO_3 and Na_2SO_4 was investigated in Experiment 7. The experiments are described and the basic solubility data presented in Appendix II. Material balances are given in Appendix III.

Thiosulfate is quite soluble in black liquor. Three of the runs showed negligible thiosulfate in the solid phase. The run with Liquor E was indicated by material balance as marginally saturated. Only the run with Liquor G showed definite evidence of precipitated thiosulfate. This was at a thiosulfate level of 16.5% on the solids and a liquor solids content of 59%. This is a concentration of about 24 g $Na_2S_2O_3$/100 g H_2O.

Thiosulfate did not appear to exert the same effect on Na_2CO_3 and Na_2SO_4 solubility as other sodium salts. Material balances indicated relatively small amounts of solid phase present. The results of analyzing these data in terms of the equivalent "NaOH" method are presented in Table IX. The measured values tend to run about 30-35% higher than expected, although allowance must be made for the fact that the solids content is 57 to 59%. It appears that the deviations from prediction are slightly higher than could be accounted for by the liquor solids effect alone. This is in agreement with the observation that thiosulfate is slightly less effective than other sodium salts in driving Na_2CO_3 and Na_2SO_4 from solution.

TABLE IX

ANALYSIS OF SOLUBILITY DATA FOR EXPERIMENT 7

Sample	Total Solids	$Na_2S_2O_3$, % on solids	"NaOH," % on solids	$Na_2CO_3 + Na_2SO_4$ Measured	$Na_2CO_3 + Na_2SO_4$ Predicted	Meas.-Pred. Predicted
7-C-1	56.9	16.4	25.8	12.9	9.6	34.4
7-C-2	57.2	17.1	26.1	12.9	9.35	38.0
7-E-1	58.8	12.8	26.0	10.0	7.6	31.6
7-G-1	59.1	16.5	26.2	9.9	7.4	33.8
7-H-1	58.8	13.8	24.0	11.7	8.8	33.0

Effect of Liquor Type

One of the objectives of this study was to try to determine how liquor composition affected solubility. Although the sodium content of the liquor is by far the most important variable, other components can also play a role. Some differences were observed in the behavior of the different liquors used in this study. In so far as the solubility of Na_2CO_3 and Na_2SO_4 is concerned, these materials were more soluble in some liquors than in others. In order to put liquor composition on a semiquantitative basis, it is convenient to rate the

solubility performance of a given liquor with respect to the average behavior. This is done on an arbitrary scale of 1 to 5 with 1 being a low solubility, 3 average, and 5 highest. The comparison is made on the equivalent "NaOH" basis so that the effect of total sodium variations is accounted for. The results of this comparison of the data are given in Table X. It can be seen that overall, the solubilities are highest in Liquor A and lowest in Liquor E. There is no obvious reason why this should be so, they are both softwood kraft mills with unoxidized liquor. The inorganic compositions of these two is not that different.

TABLE X

COMPARISON OF BEHAVIOR OF DIFFERENT LIQUOR

	Liquor								
Expt.	A	B	C	D	E	F	G	H	I
3	4	5	1	3	4	3	3	2	
4-1	4	3	3	3	3	4	4	4	
4-2	3	1	1	3	2	3	3	3	
4-3	3	1	2	3	1	2	3	3	
5	4		2						
6-1			3	3	5	3	4		
6-2			4	2	1	4	4		
7			4		2		3	3	
8	3		3	4	1			5	
9	3		3	3	1			3	
12		3		4		4	1		3
13	5		3	3			3	4	
Av	3.63	2.6	2.64	3.10	2.22	3.29	3.11	3.38	3

In order to get additional information on how the organic components affect Na_2CO_3 and Na_2SO_4 solubilities, Experiment 15 was carried out. In this experiment, solubilities of Na_2SO_4 and Na_2CO_3 were determined in a high concentration sucrose solution, a lignin rich liquor and a lignin poor liquor. The lignin rich solution was obtained by adding HCl to Liquor I, filtering off the precipitate and then treating the solids with caustic. The lignin poor liquor was prepared from the filtrate. The results are given in Appendix II.

In order to interpret the data from Experiment 15, it is helpful to analyze it in terms of the equivalent "NaOH" hypothesis. This is done in Table XI.

TABLE XI

ANALYSIS OF SOLUBILITY DATA FROM EXPERIMENT 15

Sample	Solids	"NaOH," % on solids	Measured Na_2CO_3+Na_2SO_4	Predicted Na_2CO_3+Na_2SO_4	Meas.-Pred. / Predicted, %
Sucrose	81.2	0	7.1	9.0	-21
High lignin	49.0	50.8	10.2	7.7	32.5
Low lignin	44.5	27.2	21.7	19.7	10

The solubility in the sucrose solution is about 20% less than expected from Green and Frattali's data on Na_2CO_3+Na_2SO_4 solubility in water. However, the solids content of the solution (in this case only) was calculated from the inputs and not measured. If the actual solids content were slightly higher (85%), there would be almost exact agreement between the measured and predicted solubilities. In any event, it appears that the presence of large amounts of sugars has very little effect on the solubility of Na_2CO_3 and Na_2SO_4 even at very high solids.

The solubility in the high lignin liquor is nearly 33% greater than expected, while that in the low lignin liquor is only 10% greater. This would indicate that the presence of dissolved lignin helps solubilize Na_2CO_3 and Na_2SO_4. This could happen in a number of ways. Perhaps the most likely is that the lignins bind up some of the sodium in the liquor so that it is not available for driving Na_2CO_3 and Na_2SO_4 from solution.

It is not clear that the differences in solubility associated with the various liquors used in this program can be ascribed to variations in lignin content. With the predominantly softwood liquors (A, C, E, F), high values of "precipitated solids" and methoxyl were found for Liquor A, high "precipitated solids" and lower methoxyl for Liquor F, and low "precipitated solids" and methoxyl for Liquors C and E. If these are taken as indicative of the amount of lignin present, there is a correspondence to the relative solubilities which were A > F > C > E. A similar relation is not evident in the liquors containing substantial amounts of hardwood substances.

Summary of Na_2CO_3 and Na_2SO_4 Behavior

The major variable affecting the solubility of Na_2CO_3 and Na_2SO_4 in black liquor is the sodium content of the liquor. To a first approximation, all of the sodium in the liquor (other than that present as Na_2CO_3 and Na_2SO_4) may be considered as NaOH, and the solubilities determined from the published data of Green and Frattali for the Na_2CO_3-Na_2SO_4-NaOH-H_2O system. This is valid for liquor solids contents below about 50%. Above 50% solids, Na_2CO_3 and Na_2SO_4 are more soluble than expected. The increased solubility seems to vary nearly linearly with solids content and is 35-40% greater than expected at 65% solids.

Sodium carbonate and sodium sulfate are the only two sodium salts likely to precipitate from black liquors. Sodium chloride and sodium thiosulfate are much more soluble in black liquors. The NaCl affects the solubility of Na_2CO_3 and Na_2SO_4 in proportion to its sodium content. Thiosulfate does not have as large a salting-out effect on Na_2CO_3-Na_2SO_4.

Temperature has only a weak effect on the solubilities of Na_2CO_3 and Na_2SO_4. No significant effect was found over the range of 100 to 120°C, and there was only about 10% reduction in the solubilities in going from 120 to 140°C.

The composition of the solid phase in equilibrium with solutions saturated in Na_2CO_3 and Na_2SO_4 is affected by liquor solids content. At lower solids contents, a sulfate rich solid phase somewhat close to burkeite in composition is formed as pected. At higher solids contents, the solid phase contains more Na_2CO_3 than would be expected from the solution phase composition.

APPLICATION OF RESULTS

In order for the findings of the previous section to be useful, they must make it possible to predict solubility behavior from knowledge of the composition of the liquor. The predictive requirement can be divided into two parts:

1. Prediction of the onset of saturation — the liquor solids content at which Na_2CO_3 and Na_2SO_4 first start to precipitate.
2. Prediction of the extent of precipitation — the amounts of Na_2CO_3 and Na_2SO_4 in solution and as solid phase at any specified liquor solids content.

It is necessary to describe a specific procedure for meeting these requirements.

The minimum information needed regarding liquor composition is the Na_2CO_3 content, the Na_2SO_4 content and the total sodium content. These would normally be expressed as weight % on the liquor solids. These values are considered to be known in the discussion that follows. In order to predict the onset of saturation it is necessary to predict how much water must be present to just form a saturated solution with all of the Na_2CO_3 and Na_2SO_4 present. This could be done using the triangular diagram of Green and Frattali (Fig. 5) by the following procedure. First calculate the amount of equivalent "NaOH" as a % on the solids, then calculate the weight % of Na_2CO_3 and "NaOH" on a Na_2CO_3-Na_2SO_4-"NaOH" basis, read the % dissolved solids from Fig. 5, compute the water to (Na_2CO_3+Na_2SO_4+"NaOH") ratio, and from the sum of Na_2CO_3+Na_2SO_4+"NaOH" on the liquor solids compute the solids content. Since the solubility of Na_2CO_3 and Na_2SO_4 is also a function of liquor solids content, it would be necessary to iterate over the last two steps. This is a very tedious procedure. To avoid the need for doing this, the solubility relations have been manipulated so that the critical liquor solids content for the onset of Na_2CO_3+Na_2SO_4 precipitation can be read directly from the known composition of the liquor. This is given in Fig. 14.

Figure 14 is based directly on the solubility data of Green and Frattali as expressed in their triangular diagram assuming all sodium in the black liquor (other than the Na_2CO_3 and Na_2SO_4) acts as NaOH. A correction factor is applied to account for the fact that solubilities are greater than expected at high liquor solids contents. It was assumed that no correction is needed below 50% solids and that the correction is a linear function of

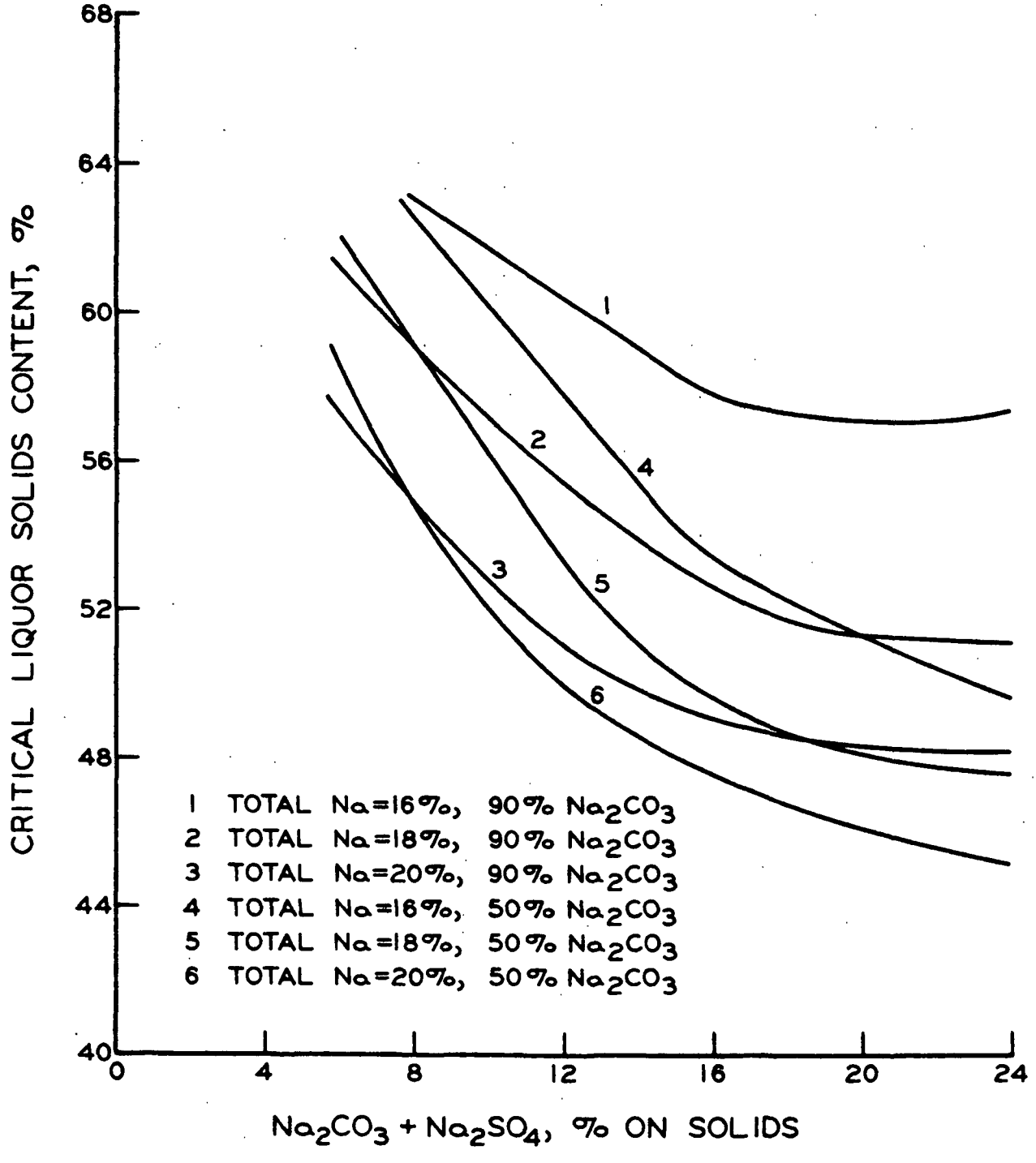


Figure 14. Prediction of Critical Liquor Solids Content for Saturation

solids above this point. It was assumed that the solubility is 35% higher than expected at 65% solids.

Figure 14 shows the critical liquor solids content as a function of the total amount of Na_2CO_3+Na_2SO_4 present. The liquor is assumed to be characterized by the total amount of Na_2CO_3 and Na_2SO_4 present, the total sodium content and the relative proportions of Na_2CO_3 and Na_2SO_4. It is seen that the critical solids content decreases as the total sodium content or the Na_2CO_3+Na_2SO_4 content increases. Increasing the sulfate proportion tends to lower the critical solids content when large amounts of carbonate and sulfate are present. The opposite is true when Na_2CO_3+Na_2SO_4 is low as can be seen by the crossing of the curves in this region (2 and 5, and 3 and 6 in Fig. 14).

The use of this figure may be illustrated with a hypothetical liquor containing 9% Na_2CO_3, 1% Na_2SO_4 and 18% total Na. In this case x-coordinate is 10% and the proportion of Na_2CO_3 is 90%. Thus, Curve 2 is applicable and the critical solids content is 57.2%. Thus, it should be possible to concentrate this liquor to 57.2% solids before precipitation of Na_2CO_3 or Na_2SO_4 would begin.

Linear interpolation may be used to estimate the critical concentration for those liquors not fitting the six curves drawn. For example, a liquor containing 17% total Na, 10.2% Na_2CO_3 and 5.8% Na_2SO_4 (total Na_2CO_3+Na_2SO_4 = 16% and proportion is 70% Na_2CO_3). The best procedure is to interpolate on one variable at a time. For example, interpolating between Curves 1 and 2 to determine the value for 17% total Na and 90% Na_2CO_3 (55.1%), and then interpolating between Curves 4 and 5 to determine the value for 17% total Na and 50% Na_2CO_3 (51.5%). The final interpolation is between these two points to

bring it to 70% Na_2CO_3 (53.3%). Thus, the critical solids content is 53.3% solids. A similar result would be obtained if the first interpolation was over the proportion of carbonate and the second over the amount of total sodium.

The prediction of the extent of precipitation can be carried out by straightforward procedures. In this case it is necessary to predict the amount of Na_2CO_3 and Na_2SO_4 which will dissolve in a liquor of a given solids content. The basic procedure is to determine the amount of non Na_2CO_3-Na_2SO_4 sodium in the liquor, relate it to the amount of water present, read the concentration of soluble Na_2CO_3+Na_2SO_4 relative to water, correct it for the high solids effect, and translate it to the basis of percentage on liquor solids. Figure 15 is drawn from Green and Frattali's data to facilitate this calculation. The x-coordinate is that sodium in the system which is not Na_2CO_3 or Na_2SO_4.

The calculation procedure may be illustrated with a hypothetical liquor analyzing 8.4% Na_2CO_3, 3.6% Na_2SO_4 and 18% total sodium. The problem is to determine how much Na_2CO_3 and Na_2SO_4 would precipitate in concentrating the liquor to 60% solids. The method is as follows:

Step 1: Calculate the effective sodium content by subtracting the sodium in the Na_2CO_3 and Na_2SO_4 from the total sodium.

$$Na = 18 - \frac{23}{53} \times 8.4 - \frac{23}{71} \times 3.6 = 13.2$$

Step 2: Express the sodium concentration on the basis of the amount of water present.

$$\frac{Na}{100\ H_2O} = 13.2 \times \left(\frac{60}{100-60}\right) = 19.8$$

Step 3: Read the soluble Na_2CO_3+Na_2SO_4 concentration from Fig. 15.

From 70% Na_2CO_3 curve, concentration = $\frac{8\ g\ Na_2CO_3+Na_2SO_4}{100\ g\ H_2O}$

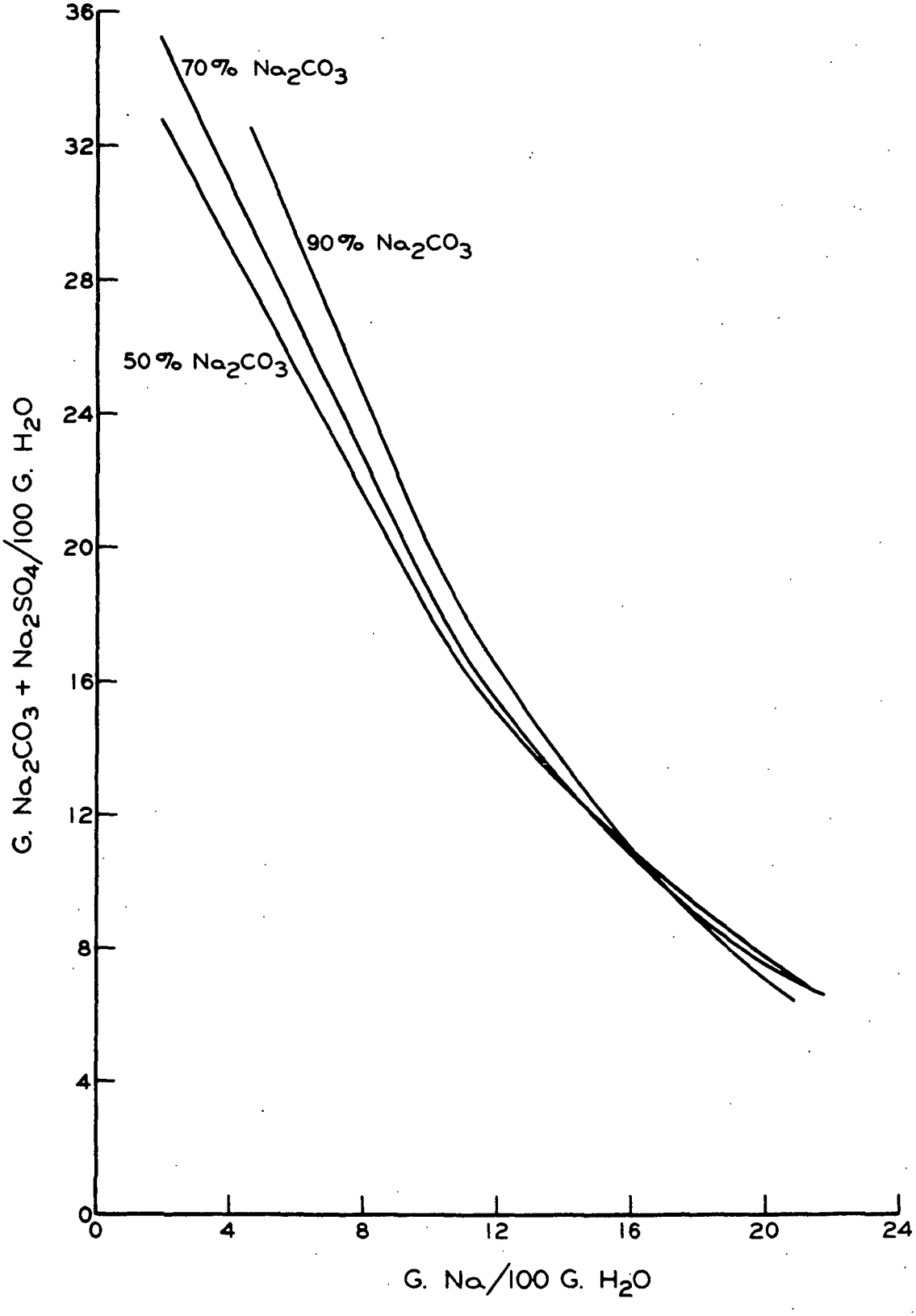


Figure 15. Working Curve for Calculation of Carbonate-Sulfate Solubilities in Black Liquor

Step 4: Correct the solubility read from Fig. 15 for the fact that measured solubilities are greater than predicted in high solids liquors. It may be assumed that no correction is needed for liquor solids below 50%. Above 50% solids, the predicted solubility should be increased by an amount given by % increase = 7/3 (solids content - 50%). At 60% solids, % increase = 23.3%. Thus, the actual soluble concentration is $\frac{9.86 \text{ g } Na_2CO_3+Na_2SO_4}{100 \text{ g } H_2O}$, (1.233×8)

Step 5: Convert the carbonate-sulfate solubility back to the basis of % on liquor solids

$$9.86 \times \frac{(100-60)}{60} = 6.58\% \text{ soluble } Na_2CO_3+Na_2SO_4$$

Thus, the extent of precipitation is given by $(\frac{12-6.58}{12}) \times 100\%$ or 45%. Of the total Na_2CO_3 and Na_2SO_4 originally present, 45% will be found as solid phase.

Analysis of Scale Samples

Samples of actual evaporator scales (and of the liquors used) were obtained and analyzed in order to demonstrate a relationship between the solubility data obtained in this study and the scaling problem. Two different scales were obtained. One sample was sent by Mill E at the same time as the liquor sample was sent. Later on, liquor and scale samples were obtained from another mill and analyzed as described under Experiment 11.

The scale sample from Mill E was taken from the first effect of a three-effect concentrator. Liquor solids in this effect are reported to average 50% while temperatures reach 300°F (150°C). The scale sample was analyzed according to the same procedures used for other samples in this program and found to have the following composition:

Sample	Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
Mill E scale	97.6	59.3	26.3	0.6	30.8	6.1	17.2

It should be noted that Na_2SO_4 accounts for essentially all of the sulfur found in the sample, and the sum of the Na_2CO_3 and Na_2SO_4 account for slightly more than the total sodium found. These data clearly indicate that the scale problem in this particular case is a Na_2CO_3-Na_2SO_4 precipitation problem. The small amount of organic found is probably just liquor imbedded within the scale as it forms.

It is worthwhile to see if the data obtained on solubility limits correlates with a scale of this type. Analysis of Liquor E gave the following composition:

Sample	Na_2CO_3	Na_2SO_4	Na_2O	Na_2S	NaCl	Total Na	Total S
Liquor E	8.5	2.1	6.0	5.2	0.4	18.9	3.7

It is of interest to note that this liquor had a high total sodium content (relative to other liquors used in this program) and might be expected to have Na_2CO_3-Na_2SO_4 precipitation problems. It is instructive to calculate the extent of precipitation expected here. The governing liquor parameters are as follows:

$$Na_2CO_3+Na_2SO_4 = 8.5 + 2.1 = 10.6\% \text{ on solids}$$

$$\% Na_2CO_3 = \frac{8.5}{10.6} \times 100\% = 80\%$$

$$\text{Effective Na} = 18.9 - \left(\frac{23}{53} \times 8.5 + \frac{23}{71} \times 2.1\right) = 14.5\% \text{ on solids}$$

At 50% solids, water present = solids present

Thus, effective Na concentration = 14.5 g Na/100 g H_2O

From Fig. 15, the carbonate-sulfate concentration = 12.6 g/100 g H_2O. At 50% solids this would amount to 12.6% on the solids. Now, it was found in this study that the solubilities of Na_2CO_3 and Na_2SO_4 were relatively independent of temperature from 100 to 120°C, and then decreased by about 10% from 120 to 140°C. Extrapolating this trend, it might be assumed that the solubilities at 150°C (300°F) are 15% lower than shown in Fig. 15. If this is true, the predicted saturation concentration for this liquor at 50% solids and 300°F would be 10.7% on the solids. This is essentially the same as was found by analysis, and indicates that saturation conditions could easily have been reached in the first effect of the concentrator from which the scale sample was obtained.

The phase distribution behavior may also be considered. The proportion of Na_2CO_3 in the liquor is 80% while that found in the scale was about 69%. Using Fig. 12, it is seen that an extent of precipitation of about 50% is needed to give this distribution. It is unlikely that this should have occurred in the first effect of the concentrator (the predicted extent of precipitation is 40% at 55% total solids for this liquor). However, it should be borne in mind that there was a definite tendency for solid phases to be richer in Na_2CO_3 than expected throughout this study. It is of interest to note that when this liquor was concentrated to 65% solids in Experiment 3, the solid phase was found to contain 76% Na_2CO_3.

The scale samples obtained from the other mill were taken from the first and second effects of a conventional multiple-effect evaporator system. Most of the deposits were found in the first effect which operates at 250°F (120°C) and a solids content of 45-50%. Two samples of liquor from this mill were also obtained, one containing some NSSC liquor and one without NSSC liquor. The sample with NSSC liquor was a four-day composite when both kraft and NSSC

pulp were being produced at a production ratio of 10 to 1. The other sample was a four-day composite when NSSC pulp was not being produced.

The results of analyzing these samples are given in Appendix II under Experiment 11. The relevant information is summarized as follows:

Sample	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
Liquor with NSSC	11.1	4.5	5.1	18.5	2.9	66.1
Liquor without NSSC	11.3	5.7	4.9	18.8	3.0	65.2
Composite scale	32.6	37.6	0.4	28.8	8.6	26.9

It should be noted that Na_2SO_4 accounts for essentially all of the sulfur found in the scale and that Na_2CO_3 and Na_2SO_4 together account for about 92% of the sodium. These data indicate that this scale problem is basically due to Na_2CO_3 and Na_2SO_4 precipitation. There is a definite organic content in the scale too, but it is not the major component.

The extent of precipitation expected for each of these two liquors may be calculated at 50% solids and 120°C by the procedures described previously. For the liquor containing NSSC liquor the relevant composition data are Na_2CO_3+ Na_2SO_4 = 15.6%, % Na_2CO_3 = 70%, and effective Na = 12.2%. This gives a saturation concentration of 15.2% on the solids and a degree of precipitation of about 2.5%. The data for the liquor without NSSC addition are Na_2CO_3+Na_2SO_4 = 17.0%, % Na_2CO_3 = 67%, and effective Na = 12.0%. This gives a saturation concentration of 15.3% and an extent of precipitation of 10%. It is clear that the evaporator is being operated above saturation conditions on occasion, and so scaling problems may be expected.

Relation to Scale Formation

There can be no doubt that solubility data have some bearing on evaporator scaling process. Whenever the scale is caused by substances crystallizing from a saturated solution, solubility limits have meaning and the definition of saturation concentrations would have a direct bearing on scaling. This would appear to be especially true of Na_2CO_3 and Na_2SO_4 scales.

Definition of solubility limits is not the complete answer to understanding scaling problems, but it is an important first step. The solubility limits do define the boundaries of the region where scales of this type can form. As long as conditions within the evaporator are outside the saturation region, crystallizing scales should not be present. It might also be expected that the magnitude of the scaling problem would be proportional to the extent that saturation limits are exceeded. Thus, knowledge of the variables affecting solubility limits can be very useful in determining what changes are needed to eliminate or minimize scaling problems. It can also provide a better understanding of the mechanism of scale formation. Thus, the clarification of solubility relationships in black liquors should be regarded as an important first step in the attack on scaling problems.

It should be pointed out that knowledge of the composition of scales is of only limited use in planning to resolve scaling problems. The major purpose of analysis of scales is to determine what type of scaling problem is involved (such as Na_2CO_3 and Na_2SO_4). Once this is known, it is much more important to get data on liquor compositions since this is what governs solubility, and where the changes have to be made.

The data correlation which has been developed in this study on Na_2CO_3-Na_2SO_4 solubility is of general validity. It incorporates all of the major

variables and the effects which they have on solubility. The prediction curves can be used and can be expected to be accurate within 5 to 10%. If very accurate solubility data are needed on a given liquor, it would be better to run a set of experiments on that particular liquor than to rely on the general curves.

SOLUBILITY OF $CaCO_3$ IN BLACK LIQUOR

Knowledge of the solubility limits of calcium compounds in black liquors was felt to be of value. Calcium carbonate scales have been reported by Berry (3) as one of the types of evaporator scales that can form. A certain amount of calcium can be expected to enter the liquor system. This can originate as $CaCO_3$ in the white liquor and there is normally a certain small amount of calcium present in the wood. If the Ca is present as ions in the liquor, then it would appear that the inorganic compounds of concern are $CaCO_3$, $CaSO_4$ and $Ca(OH)_2$, since carbonate, sulfate, and hydroxide ions are present in significant proportions in black liquors. Of these compounds, the substance with the lowest solubility in water at 100°C is $CaCO_3$. Thus, it was felt that its solubility would be controlling in black liquors. It is possible that calcium could be present in other forms in black liquor. This could include soluble organic complexes or as entrained insoluble substances.

This study of calcium solubilities in black liquor was limited to the study of the solubility of $CaCO_3$. Some published data on the solubilities of $CaCO_3$ in various aqueous solutions is given in Seidell (9) and can be used as a base line in interpreting results. The solubility of $CaCO_3$ in water at 100°C is given as 0.03759 g $CaCO_3$/liter or 39.2×10^{-6} g $CaCO_3$/g H_2O. In 55% solids black liquor this is equivalent to a calcium concentration of 0.00128% on the solids. The solubility of $CaCO_3$ in water is reported to be increased in the presence of NaCl and Na_2SO_4 and decreased by Na_2CO_3 and NaOH.

The solubility of $CaCO_3$ in black liquor was studied in Experiment 10. Details of the procedure and a summary of the data obtained are given in Appendix II. The amount of calcium found in the solution phase was quite small and presented analytical problems. This was complicated by the fact that the samples

contained large amounts of sodium which tended to interfere with the calcium determination. Calciums in the solution phase for Experiment 10 were determined by atomic absorption spectroscopy. Calciums in the solid samples were found by EDTA titration. Calcium contents had previously been run on the original liquors by Emission Spectrographic Analysis. The amounts of soluble calcium found in Experiment 10 and the amounts of calcium indicated to be present in the original liquors are summarized in Table XII.

TABLE XII

SUMMARY OF DATA ON CALCIUM SOLUBILITY

Sample	Soluble Ca Found, % on solids	Ca in Original Liquor, % on solids
10-C-1-L	0.0088	0.030
10-C-2-L	0.0194	0.030
10-D-1-L	0.0197	0.038
10-D-2-L	0.0203	0.038
10-E-1-L	0.0235	0.026
10-E-2-L	0.0341	0.026
10-F-1-L	0.0043	0.034
10-F-2-L	0.0043	0.034
10-G-1-L	0.0168	0.030
10-G-2-L	0.0182	0.030
10-A-3-L	0.0245	0.033
10-B-3-L	0.0104	0.033
10-H-3-L	0.0328	0.059
10-I-3-L	0.0333	?
10-G-3-L	0.0174	0.030

It is evident that there are few patterns in this data. However, some conclusions can be drawn. The solubility of calcium in the black liquors is about one order of magnitude higher than would be expected based on the solubility of $CaCO_3$ in water. The only exception is Liquor F in which the solubility is only three times higher than expected. There is also a definite trend for the soluble calcium to increase with time. This is seen in the 1-2 experiments in which the concentration is higher in Sample 2 than in Sample 1. Again, the only exception is Liquor F.

It would appear that the most reasonable explanation of these data is that the calcium can react slowly with some of the organics present in the liquor to form a soluble complex. If this is true, data on the solubility of calcium in inorganic solutions would not generally be applicable to spent liquors. It might also be expected that there could be large differences in solubilities between individual liquors. The amounts of soluble calcium found were quite small and it would appear to be difficult for calcium carbonate scales to form by precipitation of $CaCO_3$ from solution. It is more likely that such scales are formed by the incorporation of entrained insoluble $CaCO_3$ in the scale as it forms.

PRECIPITATIONS OF ORGANICS

The inorganic substances discussed in the previous sections are only part of the evaporator scaling problem. Organic compounds can also be involved in the formation of deposits on heat transfer surfaces. These could include soaps, alkali lignin, products of condensation reactions and salts of saccharinic or other organic acids. The behavior of the organic constituents was also studied in this project.

NATURE OF PROBLEM

The soaps originate from the fatty acids and resin acids in the wood. They are present in the liquor as an association colloid or micelle. The micelle consists of an association of many fatty acid or resin acid molecules in a configuration such that the organic portions are grouped inward and the polar, acid groups are directed outward. Other organic compounds can be solubilized by these micelles. The polar groups are basically responsible for colloidal stability and the resultant solubility in the liquor. One of the properties of soap solutions is that as the concentration of electrolytes in the solution is increased to a certain level, a soap "precipitate" will form. Since many of the inorganic compounds in black liquor are electrolytes, concentrating a black liquor will also cause the soaps to precipitate. Soap precipitation occurs at relatively low levels of liquor solids content. This is the basis for their removal from the liquor as part of the multiple-effect evaporator sequence. Under these circumstances it appears that the amount of soap present in high solids liquor is mainly a function of the soap removal system. All of the liquors involved in this study were obtained from points at the end of the conventional multiple-effect evaporator system and may be presumed to be generally low in soap content.

The alkali lignin in the liquor is present as a macromolecular colloid. The lignin polymer in the liquor from an alkaline process typically contains from 3 to 10 phenylpropane monomer units and has a molecular weight range from 500-2000. The macromolecule contains phenolic hydroxyl and carboxylic acid groups and these are considered to be the main solubilizing groups. The solubility is affected by whether these groups are in the salt or acid form, and, hence, by pH. Lignin precipitation may readily be brought about by lowering the pH of an alkaline liquor. The colloidal stability of alkali lignin is also reported to be influenced by electrolyte concentration (8). If this is an important factor, then it might be expected that there would be a tendency for lignin precipitation at high solids contents since increasing total solids concentration would also increase electrolyte concentrations. The extent of and governing factors for lignin precipitation was considered to be an important part of this study.

Rubberlike deposits on evaporator tubes have been reported. These have been attributed to condensation reactions occurring under the conditions existing in the evaporator. They are reported to be more likely to occur under conditions of high temperature and high alkalinity. It appears that these reactions are generally considered to involve the alkali lignin and be analogous to phenol-formaldehyde condensations. However, the alkali lignin in the black liquor is already fairly condensed as a result of reactions taking place in the cook, and it is not clear that it remains able to take part in significant polymerization reactions.

Most of the carbohydrate material dissolved in the cook is present in the liquor as the salts of saccharinic acids. The sodium salts of these materials are generally considered to be quite soluble as are the sodium salts

of the low molecular weight acids such as formic and acetic. Attention was paid to the possibility that these materials could precipitate in concentrated liquors during this program, but it was considered to be unlikely.

This study was based on the measurement of equilibrium solubility conditions. This means measurement of the concentrations existing in the liquor when a reversible interchange of material between a solid phase and the liquor occurs. This is implicit in the concept of saturation. There is some question as to the applicability of these concepts to organic precipitations from black liquors. Certainly deposits formed by condensation reactions cannot fit this criterion. The key concept is that of reversibility. Whatever change is used to bring about precipitation (such as concentrating the liquor), the material must go back into solution when the procedure is reversed (liquor is diluted). The behavior of the lignin macromolecular colloid is expected to be reversible. The behavior of the soap colloid may not be reversible. In fact, some of the soap in the liquors used in this study may be present as entrained solid phase.

Determination of saturation concentrations rests on the ability to measure the concentration of the component involved. This is relatively straightforward for the inorganic species which were studied because they exist as well-defined compounds which can be measured. This is not the case with the organic constituents. These are a complex mixture of many different compounds. The organic fraction of the liquors can be characterized by certain tests, but its exact definition defies analysis. This is especially true of the organics of major interest in this study, the alkali lignin. The inability to make exact determinations of the amount of lignin present in samples made it impossible to look at organic solubility limits with the same degree of precision as for

Na_2CO_3-Na_2SO_4. The approach which was taken was to look at the difference between the total solids found and the amounts of known inorganic substances. This difference was assumed to be the organics. When a significant amount of organic was found in the solids (based on both the calculated solid phase composition and the extent of precipitation indicated by material balance) the nature of the liquor involved would be considered in determining the likely composition. A series of tests were run on the original liquors to help characterize them. These included potential tall oil (petroleum ether solubles) which is a measure of the soap content; the weight percentage of liquor solids which could be precipitated with HCl, methoxyl and phenolic hydroxyl, all related to the lignin content; and the amounts of acetate and formate present. These data are given in Appendix I.

DATA ON ORGANIC PRECIPITATION

The major intent of this program was to develop information on the extent of the organic precipitation problem. In general, it was found to be much less than the Na_2CO_3-Na_2SO_4 problem. In practically all experimental runs, much more carbonate and sulfate was found in the solid phase than organics.

The extent of organic precipitation can be evaluated by considering the organic percentages in the "true solid" phase in the data given in Appendix II. It is worthwhile to consider the lower liquor total solids runs first. These include Experiments 4, 5, 6, 7, 8, and 9. In Experiment 4, the organic in the solid phase is negligible for Liquors B, C, D, E, and G. It runs from 20-35% for Liquor A, 5-15% for Liquor F, and 10-15% for Liquor H. It is of interest that these same three liquors had the highest values of potential tall oil (see Appendix I), namely, 3.7% for Liquor A, 1.2% for Liquor F, and 0.7%

for Liquor H. Thus, it appears reasonable to conclude that the observed organic precipitation in Experiment 4 is due to precipitation of residual soaps in the liquor. The same is true of Experiment 5, in which Liquor A showed 10-15% organic and Liquor C gave 3-7%. Organic precipitation was essentially negligible in Experiments 6 and 7 in which NaCl and $Na_2S_2O_3$ were added to the liquors (even though the data summary for Experiment 7 shows high organic levels in the solid phase, the material balance indicates that very little solids are present). These runs involved Liquors C, D, E, F, G, and H. Thus, the addition of relatively large amounts of strong electrolytes at 57-58% total solids did not cause the precipitation of significant amounts of organics. The data for the higher temperature runs, Experiments 8 and 9, also fit this picture. The only two liquors which showed significant organic in the solid phase were Liquors A and H, which have relatively high values of potential tall oil.

It appears that all of the data on organic precipitation for Experiments 4 through 9 can be explained by assuming the precipitated organic to be soap. There is no significant evidence for lignin precipitation. Confirmation of sorts for this position was obtained by a more detailed analysis of some of the material from a Liquor A solid sample. There was a tendency for a scum to form in all of the solid samples from Liquor A even when they were diluted to the 5% level used in the analyses. A sample of this scum was subjected to more detailed analysis and was found to contain resinous material and a rather large amount of hydrocarbon oil. The hydrocarbon was apparently solubilized by the soap. No evidence for ligninlike compounds was found in this scum sample.

The extent of organic precipitation relative to Na_2CO_3 and Na_2SO_4 was greater in Experiments 3, 12, and 13. These were generally higher solids runs

and are considered to be the runs where lignin precipitation would be most likely to occur. A summary of the relevant data is given in Table XIII. This includes the % organic in the solid phase, the amount of Na_2CO_3+Na_2SO_4 found and the organic precipitated as a percentage of total solids as indicated by material balance.

TABLE XIII

SUMMARY OF ORGANIC PRECIPITATION DATA FOR EXPERIMENTS 3, 12, AND 13

Run	Liquor Solids, %	Organic, % of solid phase	Na_2CO_3+Na_2SO_4, % of solid phase	Precipitated Organic, % of total solids
3-A-1	63.6	47.5	43.0	3.88
3-B-1	69.7	23.0	59.7	1.53
3-C-1	57.9	6.4	89.2	0.17
3-D-1	62.6	23.6	73.4	2.76
3-E-1	64.7	22.5	72.1	1.75
3-F-1	58.1	10.9	82.8	0.23
3-G-1	64.8	6.8	94.3	0.55
3-H-1	58.7	13.2	75.1	0.00
12-B-1	64.9	23.5	79.4	2.07
12-D-1	65.5	24.8	68.3	2.57
12-F-1	65.6	22.5	71.3	1.80
12-G-1	63.9	16.1	82.2	1.25
12-I-1	64.7	6.9	87.5	0.60
13-A-1	59.1	34.4	61.6	0.00
13-C-1	54.8	14.1	80.7	1.60
13-D-1	57.7	14.4	82.8	1.09
13-G-1	57.6	15.0	79.5	1.42
13-H-1	58.4	31.6	58.8	1.73

Examination of the data in Table XIII shows that even under severe conditions (up to 65% solids) organic precipitation tends to be much less than Na_2CO_3 and Na_2SO_4 precipitation. The influence of soap concentration is also apparent. Highest values of organic percentages are shown by Liquor A which had the highest value of potential tall oil. It is likely that soaps constitute

a significant fraction of the precipitated organic in all of the runs shown in Table XIII. It is possible that some lignin precipitation may have occurred in these experiments. If so it only involves about 1% of the total liquor solids. Lignin precipitation at these levels is not readily detectable by the procedures used in this study. If rigorous definition of the limits for lignin precipitation is desired a different approach would have to be taken. However, it is not obvious that this information is critical to the evaporator scaling problem. It can be concluded that, to the extent that the liquors used in this study are representative of the industry, lignin precipitation is a minor part of the scaling problem. However, it is possible that organic deposits may form in evaporators by other means.

EXPERIMENT 14

The above discussion has been concerned with organic precipitation which was induced either by concentrating the liquor or by the addition of neutral or alkaline electrolytes. It is known that pH has a large effect on the stability of the colloidal lignin. Experiment 14 was designed to examine the extent of precipitation of liquor solids when sufficient acid was added to neutralize the Na_2O present in the liquor and to determine if this precipitation was reversible on addition of enough NaOH to bring the Na_2O back to the original level. The description of this experiment and a summary of the solubility data obtained are given in Appendix II. Material balances over these runs are given in Appendix III. Excellent material balances were obtained.

The material balances show that a large amount of material (15 to 25% of the total solids) is precipitated upon addition of the acid. This precipitated material may be seen to be almost entirely organic. This, of course, was exactly what was expected and illustrates that the experimental techniques

employed would detect lignin precipitation if it occurred to any appreciable extent. It is also clear that essentially all of this material goes back into solution upon addition of the NaOH. The only run with any definite indication of solid phase is 14-C-2, and in this case the solid phase is Na_2CO_3 and Na_2SO_4. Thus, lignin precipitation due to lowering of the pH is completely reversible upon raising the pH back to the original level. This behavior is in accordance with expectations for a macromolecular colloid of this type.

An attempt was made in Part II of Experiment 14 to add HCl to a liquor and follow the change in viscosity as the pH dropped. This experiment was not very successful because the viscosity did not change much. One problem was dilution of the liquor as acid was added. The total amount of HCl added was sufficient to neutralize about 1/4 of the Na_2O originally present in that liquor.

INTERPRETATION OF ORGANIC DATA

The most likely organic compounds to precipitate during the concentration of black liquor are soaps. Almost all of the organic precipitation found in this study could be attributed to residual soap content in the liquors. Evidence for lignin precipitation due to concentration of the liquor or electrolyte addition was marginal. If any lignin precipitation did occur under these conditions it was much less than the simultaneous precipitation of Na_2CO_3 and Na_2SO_4. On this basis lignin precipitation does not appear to be a major problem in evaporator scaling. Lignin can be readily precipitated by addition of acid. This effect is reversible upon readdition of caustic. Thus, if lignin is precipitated by the addition of an acidic material to the liquor, the effect can be overcome by adding alkali. Final pH is the determining factor. There was no evidence for precipitation of salts of saccharinic acids.

GENERAL CONCLUSIONS

The major solubility problem, as such, in black liquor is the solubility of Na_2CO_3 and Na_2SO_4. With the exception of lignin precipitation caused by major acidification of the liquors, these were the major precipitants in practically every experiment in the entire study. In so far as evaporator scaling problems are manifestations of basic equilibrium solubility effects, the major scaling problem is due to Na_2CO_3 and Na_2SO_4.

A correlation of Na_2CO_3 and Na_2SO_4 solubilities that is generally valid for all alkaline process black liquors has been found. It is believed to be accurate within 5 to 10%. It is based upon the application of the solubility data of Green and Frattali for the Na_2CO_3-Na_2SO_4-NaOH-H_2O system to black liquors. The sodium content of the black liquor (less the sodium present as Na_2CO_3 and Na_2SO_4) is identified with the NaOH. Values of the solubility are then corrected for a total liquor solids effect to take into account the fact that solubilities in high solids black liquor are greater than expected. The correlation is summarized in Fig. 14 and 15 in the text.

The major liquor composition variable affecting the solubility of Na_2CO_3 and Na_2SO_4 is the total sodium content. The next most important variable is liquor solids content. Temperature does not have an appreciable effect over the range 100-120°C (212-250°F). The solubility does drop about 10% in going from 120 to 140°C (250-280°F). Sodium chloride and sodium thiosulfate are quite soluble in black liquors at least up to 10% on the solids. Their main effect is to drive out Na_2CO_3 and Na_2SO_4. The thiosulfate has a lesser tendency to do this than the chloride.

An attempt to determine solubility limits for $CaCO_3$ in black liquor was unsuccessful, because the results fit no logical pattern. It was found that the solubility in black liquor was about one order of magnitude higher than expected based on the solubility of $CaCO_3$ in water. There was some evidence for slow formation of a soluble calcium complex in some of the liquors.

Most of the organic that precipitated could be correlated with the soap content of the liquors. Evidence for lignin precipitation in concentrated liquors was marginal. If lignin precipitation is occurring during evaporation to 65% solids, it is small compared to simultaneous precipitation of Na_2CO_3 and Na_2SO_4. Acidification of the liquor, on the other hand, did lead to significant lignin precipitation. This went back into solution upon addition of caustic. Thus, the precipitation of lignin by lowering pH is a reversible process. In general, it would appear that evaporator scaling problems due to equilibrium solubility effects of organics are much less important than those due to Na_2CO_3 and Na_2SO_4. The exceptions would be liquors with high soap contents and lowering the pH of the liquor. If lignin precipitation is a significant part of the evaporator scaling problem, this would indicate the scaling to be a nonequilibrium process which would have to be attacked by other techniques than those used in this study.

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APPENDIX I

CODING AND DESCRIPTION OF LIQUORS USED IN STUDY

A total of nine different liquors were obtained from sponsoring mills for use in this study. They were given the code letters A through I for identification purposes. A description of the origin and nature of these liquors follows.

Liquor A: This liquor was obtained from a southern linerboard mill. Pulp production is kraft only. The liquor is unoxidized taken directly out of the multiple-effect evaporators. Wood species is southern pine, primarily slash pine. Wood is about 95% softwood.

Liquor B: This liquor was obtained from a northeast bleached kraft mill. This is unoxidized liquor directly from the multiple-effect evaporator. Wood is about 30% softwood and 70% hardwood. Softwoods are white pine and hemlock. Hardwoods are primarily maple and beech along with some birch, ash, elm, and cherry.

Liquor C: This liquor was obtained from a southern board mill producing corrugating and liner. Pulp production is about 82% kraft and 18% NSSC. The liquor is unoxidized and collected from the multiple-effect evaporator discharge. Wood on the kraft side is principally pine, but does contain some (<5%) hardwood. Spent liquor from the hardwood NSSC mill is used as kraft digester fill and as dilution or shower flow to the first stage washers. The liquor was soap skimmed.

Liquor D: This liquor was obtained from a southeastern bleached kraft mill. The liquor is unoxidized. The liquor is from a production of about 38% pine pulp and 62% hardwood pulp. The mill does not segregate the hardwood and pine liquors. The pine is southern yellow pine and the hardwood is about 50% gum and 50% oak.

Liquor E: This liquor was obtained from a northwest kraft mill. The liquor was taken following multiple-effect evaporators ahead of a concentrator. The liquor is unoxidized. The wood is 100% softwood, some chip and some sawdust. About 50% of the softwoods are white and about 50% dark.

Liquor F: This liquor was obtained from a west coast kraft mill which also had some semichemical pulp production. No information was provided on sampling point, species or state of oxidation.

Liquor G: This liquor was obtained from a northeastern bleached kraft mill. The liquor was taken after the multiple-effect evaporators. The mill practiced weak black liquor oxidation with an oxidation efficiency of 78%. The wood species are a mixed hardwood, containing beech, birch, oak, maple, elm, and poplar.

Liquor H: This liquor was obtained from a southeastern kraft mill producing pine and hardwood kraft pulp and semichemical hardwood pulp. The pulp production is distributed approximately as 20% pine, 65% hardwood kraft, and 15% semichemical. The distribution of liquor solids is about pine 25%, hardwood kraft 73%, and semichemical 2%. The hardwood is mainly oak. The pine is mainly Virginia pine. The liquor was taken following the evaporators and is representative of a mixture of the three types of black liquor.

Liquor I: This liquor was obtained from a mideastern bleached kraft mill. Pulp production is about 70% hardwood and 30% softwood. No additional information was furnished on this liquor.

Data on the composition of these liquors with respect to the major sodium compounds are as follows:

Liquor	Na_2CO_3	Na_2SO_4	Na_2O	Na_2S	NaCl	Total Na	Total S
A	7.5	1.7	5.2	5.3	0.5	16.3	2.6
B	9.1	1.6	8.6	3.9	0.2	18.2	3.6
C	5.2	4.2	5.9	6.4	0.2	16.5	5.0
D	11.3	2.6	4.8	3.5	0.8	17.5	2.7
E	8.5	2.1	6.0	5.2	0.4	18.9	3.7
F	7.9	4.1	6.2	1.3	0.2	17.8	4.0
G	8.0	3.0	4.1	0.9	0.2	17.9	4.1
H	9.9	2.4	5.2	2.6	0.9	17.9	2.6
I	7.0	6.0	4.8	--	--	17.4	4.2

Data relevant to the organic contents of the liquors follow:

Liquor	Precipitated Solids	Potential Tall Oil	Methoxyl	Phenolic Hydroxyl	Acetate	Formate
A	31.2	3.7	5.2	1.2	5.4	2.1
B	24.0	0.2	5.8	1.0	7.1	1.95
C	27.2	0.5	4.8	1.1	7.3	1.5
D	24.7	0.4	5.8	1.05	8.3	1.45
E	28.0	0.4	4.5	1.15	4.0	2.9
F	30.7	1.2	4.6	1.0	5.6	1.9
G	21.9	0.3	5.9	1.1	7.7	2.0
H	23.5	0.7	5.8	0.95	8.6	1.7

All values as percentage on liquor solids.

Precipitated solids is the weight percentage of the liquor solids which are precipitated with HCl. It is taken as a measure of the lignin content of the liquor.

Potential tall oil is determined as that part of the liquor solids soluble in petroleum ether. It is a measure of the soaps remaining in the liquors.

APPENDIX II

EXPERIMENTAL CONDITIONS AND SOLUBILITY DATA

In this appendix, details of the experimental conditions and summaries of the solubility data obtained are provided for each of the experiments carried out on this project. In most of the experiments, the following code is used in presenting the results. Each individual solubility run is identified by a number-letter-number sequence. The first number is the number of the experiment, the letter designates the liquor used (see Appendix I for liquor code) and the second number identifies individual runs. The different samples within a run are identified with a second letter code: L designates a solution phase sample, S a solid phase (sludge) sample and O an original liquor sample. The letters TS designate the "true solid" phase calculated from the solution and solid sample data by correcting the latter for entrained liquor. Thus, a sample designated as 6-G-2-L is a solution phase sample from Experiment 6, using Liquor G, and is the second run in that particular sequence. Exceptions to this method of coding will be made clear in the description of the particular experiments.

With the exception of liquor total solids content, <u>all data are expressed as weight percentage on dry solids</u>. Total solids is, of course, expressed as weight percentage on a wet basis in the usual manner.

DESCRIPTION OF EXPERIMENT 1

Five vessels were loaded in the following manner:

V	W	X	Y	Z
1200 g Na_2CO_3	1200 g Na_2SO_4	1100 g NaCl	400 g Na_2CO_3	3500 g of a soda
2700 g H_2O	2700 g H_2O	2600 g H_2O	400 g Na_2SO_4	black liquor
			400 g NaCl	100 g Na_2CO_3
			2700 g H_2O	100 g Na_2SO_4

The systems were then equilibrated for 24 hours at 100°C and a solution sample of each taken. This was Set 1.

Solid NaOH was then added to each of the vessels. The amounts added were 100 g NaOH each to Vessels V, W, and X, 50 g to Vessel Y, and 30 g to Vessel Z. A second set of solution samples was then taken. Three solution samples were taken from each vessel: approximately 2 hours, 6 hours, and 24 hours after the NaOH was added.

This was followed by another round of caustic addition. The amounts added were 200 g NaOH each to Vessels V, W, and X, 100 g to Vessel Y, and 50 g to Vessel Z. A third set of solution samples was then taken. Each vessel was sampled approximately 2 hours, 6 hours, and 24 hours after the NaOH was added.

BASIC SOLUBILITY DATA FROM EXPERIMENT 1

Sample	Dissolved Solids	Na_2CO_3	Na_2SO_4	NaOH	NaCl	Total Na
1-V-1-L	29.5	99.9		0.1		41.4
1-V-21-L	29.0	91.5		8.5		47.3
1-V-22-L	29.1	90.8		9.2		42.7
1-V-23-L	29.3	90.8		9.2		43.7
1-V-31-L	27.3	69.0		31.0		49.1
1-V-32-L	27.3	69.8		30.2		52.3
1-V-33-L	27.2	69.5		30.5		50.6
1-W-1-L	28.5		100.0	0.0		32.8
1-W-21-L	27.4		90.2	9.8		32.6
1-W-22-L	26.9		90.4	9.6		33.9
1-W-23-L	26.9		90.4	9.6		30.3
1-W-31-L	24.8		67.8	32.2		41.9
1-W-32-L	24.6		66.3	33.7		41.4
1-W-33-L	24.8		66.5	33.5		43.9
1-X-1-L	26.0			0.0	100.0	41.2
1-X-21-L	27.8			9.7	90.3	41.4
1-X-22-L	26.3			10.5	89.5	43.0
1-X-23-L	28.2			9.4	90.6	40.4
1-X-31-L	29.2			28.0	72.0	48.6
1-X-32-L	29.2			27.4	72.6	47.9
1-X-33-L	29.1			28.1	71.9	49.7
1-Y-1-L	25.0	32.2	25.2	0.0	42.6	39.6
1-Y-21-L	25.5	31.3	21.0	4.9	42.8	41.7
1-Y-22-L	25.7	31.1	21.7	5.1	42.2	40.1
1-Y-23-L	25.8	30.9	20.7	5.0	43.4	38.8
1-Y-31-L	25.8	27.9	13.7	15.3	43.1	46.8
1-Y-32-L	25.7	28.0	14.2	15.5	42.2	44.0
1-Y-33-L	25.8	27.5	14.1	16.0	42.4	44.6
1-Z-1-L	58.6	4.1	1.0	5.5		11.5
1-Z-21-L	58.0	4.5	0.6	5.4		11.3
1-Z-22-L	58.2	2.8	0.7	6.5		11.7
1-Z-23-L	58.7	3.9	0.8	6.3		12.2
1-Z-31-L	60.8	3.4	0.7	7.2		12.6
1-Z-32-L	57.0	3.2	0.8	7.3		11.7
1-Z-33-L	Probe damaged					

DESCRIPTION OF EXPERIMENT 2

The liquor which was used in this experiment was a soda black liquor which was available. It analyzed at 61.4% solids and had the following composition: total sodium = 18.9%, Na_2CO_3 = 5.8%, Na_2SO_4 = 0.2%, and Na_2O = 8.4% on the solids.

The burkeite used in this experiment was prepared by dissolving 300 g Na_2SO_4 in 1000 g H_2O and 111 g Na_2CO_3 in 300 g H_2O, mixing the two solutions and evaporating off the water.

Five vessels were loaded as follows:

V	W	X	Y	Z
2800 g liquor	2800 g liquor	2800 g liquor	3500 g liquor	3500 g liquor
600 g H_2O	600 g H_2O	600 g H_2O		
200 g Na_2CO_3	250 g Na_2SO_4	250 g burkeite	200 g Na_2CO_3	250 g Na_2SO_4

These were equilibrated for 48 hours at 100°C and then sampled. The solution samples (L) were obtained with the fritted glass filters as usual. Samples of solid phase (SX) were obtained by removing liquor and solids through an ordinary glass tube.

The following materials were then added to the vessels:

V	W	X	Y	Z
250 g Na_2SO_4	200 g Na_2CO_3	100 g of 50% NaOH	250 g Na_2SO_4	200 g Na_2CO_3

The systems were then equilibrated for 48 hours at 100°C and sampled as before. A final sludge sample for solid phase determination (S) was taken when the vessels were emptied.

BASIC SOLUBILITY DATA FROM EXPERIMENT 2

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na
2-V-1-L	50.5	12.8	0.3	6.8	20.3
2-V-1-SX	53.2	14.5	0.4	7.0	20.9
2-V-2-L	50.4	9.7	1.4	7.0	19.7
2-V-2-SX	55.5	14.5	9.0	6.2	22.9
2-V-2-S	81.0	15.6	67.3	1.5	32.4
2-V-1-TSX		29.8	0.9	8.8	26.8
2-V-2-TSX		35.7	42.4	2.9	36.9
2-V-2-TS		17.4	87.7	-0.2	36.3
2-W-1-L	50.0	2.3	4.2	8.6	19.0
2-W-1-SX	55.1	5.9	14.3	6.8	20.5
2-W-2-L	50.0	9.4	1.4	7.5	20.3
2-W-2-SX	56.2	14.7	12.1	6.1	23.2
2-W-2-S	74.9	33.5	36.5	2.5	32.5
2-W-1-TSX		21.8	58.6	-1.3	27.1
2-W-2-TSX		33.6	50.0	1.2	33.6
2-W-2-TS		45.7	54.2	0.0	38.6
2-X-1-L	44.6	5.8	3.4	7.3	19.9
2-X-1-SX	50.7	5.6	4.2	7.6	20.6
2-X-2-L	46.5	5.6	3.2	9.2	20.7
2-X-2-SX	49.9	6.7	6.1	9.2	21.2
2-X-2-S	76.2	23.1	49.7	2.5	30.9
2-X-1-TSX		5.0	7.0	8.6	23.1
2-X-2-TSX		13.9	25.9	9.2	24.6
2-X-2-TS		29.6	67.0	0.0	34.7
2-Y-1-L	58.3	6.1	0.3	7.5	21.5
2-Y-1-SX	62.8	12.4	0.3	7.5	20.8
2-Y-2-L	54.0	5.4	1.5	7.4	18.5
2-Y-2-SX	65.1	13.3	8.6	6.6	21.3
2-Y-2-S	85.0	12.2	65.2	1.8	30.7
2-Y-1-TSX		42.6	0.5	7.2	17.4
2-Y-2-TSX		26.8	20.5	5.2	26.1
2-Y-2-TS		14.0	81.7	0.4	33.8
2-Z-1-L	58.5	4.0	1.8	8.0	20.8
2-Z-1-SX	62.4	5.1	2.7	7.8	20.1
2-Z-2-L	58.5	5.0	0.9	7.8	18.8
2-Z-2-SX	65.8	13.1	12.5	6.4	22.2
2-Z-2-S	81.9	16.0	62.0	2.4	30.2
2-Z-1-TSX		11.4	8.0	7.0	16.2
2-Z-2-TSX		35.2	44.1	2.5	31.5
2-Z-2-TS		21.0	89.6	-0.2	35.4

DESCRIPTION OF EXPERIMENT 3

Eight of the liquors obtained from sponsors' mills (Liquors A through H) were slowly concentrated over a 48-hour period at 100°C in the stirred vessels. Solution phase and sludge samples were taken in the normal manner. A sample of evaporator scale obtained from Mill E was also analyzed for comparison with the solid phase precipitated from Liquor E in this experiment. The water vapor driven off during the evaporation was not condensed and measured in this experiment. Termination was arbitrary.

BASIC SOLUBILITY DATA FROM EXPERIMENT 3

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
3-A-1-L	63.6	3.8	2.4	5.1	17.0	2.45	
3-A-1-S	66.9	8.7	2.5	4.8	17.7	2.55	
3-A-1-TS		39.9	3.1	2.9	22.0	3.1	47.5
3-B-1-L	69.7	5.8	1.4	6.4	17.5	3.5	
3-B-1-S	76.4	18.7	3.6	5.1	23.5	3.45	
3-B-1-TS		50.6	9.1	2.1	38.8	3.3	23.0
3-C-1-L	57.9	4.6	2.6	4.8	15.8	4.8	
3-C-1-S	79.3	23.5	36.2	2.2	28.8	9.9	
3-C-1-TS		34.1	55.1	0.8	36.1	12.7	6.4
3-D-1-L	62.6	4.3	1.7	5.0	16.1	2.4	
3-D-1-S	68.7	16.6	5.4	4.0	19.9	2.8	
3-D-1-TS		56.1	17.3	0.8	32.1	4.1	23.6
3-E-1-L	64.7	3.9	1.5	5.5	16.5	3.5	
3-E-1-S	68.2	11.3	3.8	4.9	19.0	3.6	
3-E-1-TS		54.8	17.3	1.3	33.5	4.2	22.5
3-F-1-L	58.1	7.8	2.7	4.6	16.4	3.5	
3-F-1-S	71.5	22.4	20.4	2.9	25.3	6.4	
3-F-1-TS		40.5	42.3	0.8	36.3	10.0	10.9
3-G-1-L	64.8	2.2	1.5	4.1	16.8	4.0	
3-G-1-S	78.0	29.9	17.2	1.9	26.5	5.6	
3-G-1-TS		59.9	34.4	-0.5	37.0	7.3	6.8
3-H-1-L	58.7	11.1	1.7	1.8	14.4	2.4	
3-H-1-S	77.6	38.6	10.9	1.85	29.5	3.7	
3-H-1-TS		57.8	17.3	1.9	40.0	4.6	13.2
3-E-Scale	97.6	59.3	26.3	0.6	30.8	6.1	17.2

DESCRIPTION OF EXPERIMENT 4

A series of three runs was made on each of eight different liquors. Solid Na_2CO_3 and Na_2SO_4 were added to the liquors which had been adjusted to about 45% solids content. The amounts added were 125 g Na_2CO_3 and 125 g Na_2SO_4, 75 g Na_2CO_3 and 175 g Na_2SO_4, and 40 g Na_2CO_3 and 210 g Na_2SO_4 for Runs 1, 2, and 3, respectively. These same amounts were added to all of the liquors. The amounts of liquor used were as follows:

A — 2980 g Liquor A + 420 g H_2O for each run

B — 3020 g Liquor B + 380 g H_2O for each run

C — 3030 g Liquor C + 370 g H_2O for each run

D — 3200 g Liquor D + 200 g H_2O for each run

E — 3275 g Liquor E + 125 g H_2O for each run

F — 3285 g Liquor F + 115 g H_2O for each run

G — 3380 g Liquor G + 20 g H_2O for each run

H — 3510 g Liquor H - 110 cc H_2O evaporated for each run

Each sample was prepared, brought up to 100°C, equilibrated for 24 hours and sampled in the usual manner.

BASIC SOLUBILITY DATA FROM EXPERIMENT 4

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
4-A-1-L	47.9	11.8	8.4	4.8	20.0	3.8	
4-A-1-S	57.9	13.6	19.8	3.6	21.1	5.7	
4-A-1-TS		17.3	42.9	1.1	23.3	9.5	37.6
4-A-2-L	47.0	9.2	9.9	5.05	18.5	4.1	
4-A-2-S	75.5	11.3	44.6	1.5	21.8	10.3	
4-A-2-TS		12.1	58.6	0.1	23.2	12.8	31.0
4-A-3-L	46.6	8.3	10.0	5.05	19.1	4.2	
4-A-3-S	85.7	8.7	60.0	0.75	24.8	14.4	
4-A-3-TS		8.8	68.6	0.0	25.8	16.2	21.5
4-B-1-L	46.1	12.9	6.0	7.95	20.8	4.1	
4-B-1-S	81.1	30.9	47.7	1.7	32.6	11.9	
4-B-1-TS		35.4	58.1	0.2	35.6	13.8	3.7
4-B-2-L	46.0	10.4	5.7	8.4	19.7	4.2	
4-B-2-S	83.7	24.9	60.0	1.2	31.6	13.9	
4-B-2-TS		27.8	70.9	-0.2	33.9	15.8	2.8
4-B-3-L	45.7	6.9	6.7	8.25	18.6	4.4	
4-B-3-S	84.8	20.6	64.1	1.5	32.1	14.8	
4-B-3-TS		23.1	74.5	0.3	34.6	16.7	1.9
4-C-1-L	46.3	10.3	8.2	5.4	19.6	5.4	
4-C-1-S	81.5	28.4	54.5	0.85	32.9	12.8	
4-C-1-TS		32.9	65.9	-0.3	36.2	14.6	1.1
4-C-2-L	45.7	7.3	8.3	5.55	18.3	5.6	
4-C-2-S	81.5	24.8	58.7	0.7	31.1	13.8	
4-C-2-TS		28.9	70.6	-0.45	34.1	15.6	2.5
4-C-3-L	45.2	5.7	9.9	5.5	18.5	6.1	
4-C-3-S	79.8	22.1	59.6	0.9	29.0	14.0	
4-C-3-TS		26.5	72.8	-0.3	31.8	16.1	4.7
4-D-1-L	47.3	14.9	7.6	4.8	19.7	2.4	
4-D-1-S	70.8	25.2	45.5	2.1	27.6	8.9	
4-D-1-TS		31.5	67.8	0.5	32.3	12.7	9.2
4-D-2-L	47.3	12.5	8.9	4.6	19.7	3.8	
4-D-2-S	71.1	25.0	44.3	1.5	27.4	10.4	
4-D-2-TS		32.2	64.6	-0.3	31.9	14.2	6.9
4-D-3-L	46.5	9.3	9.5	5.1	19.1	3.9	
4-D-3-S	74.8	21.8	49.0	1.7	28.5	11.5	
4-D-3-TS		27.0	65.5	0.3	32.4	14.6	8.1

BASIC SOLUBILITY DATA FROM EXPERIMENT 4 (Continued)

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
4-E-1-L	47.1	12.7	7.0	5.5	20.2	4.3	
4-E-1-S	82.5	29.2	52.2	0.85	33.3	12.3	
4-E-1-TS		33.0	62.8	-0.2	36.3	14.1	2.8
4-E-2-L	46.2	10.1	6.7	5.65	19.7	4.4	
4-E-2-S	85.0	23.9	61.8	0.75	30.9	14.3	
4-E-2-TS		26.4	71.6	-0.1	33.0	16.1	3.7
4-E-3-L	45.2	7.4	7.5	5.75	19.0	4.6	
4-E-3-S	82.3	21.7	61.0	1.1	31.6	14.1	
4-E-3-TS		24.8	72.6	0.1	34.4	16.2	2.7
4-F-1-L	48.1	13.0	7.2	4.7	20.1	4.2	
4-F-1-S	80.7	27.5	49.3	1.05	30.1	9.1	
4-F-1-TS		31.6	61.3	0.0	33.0	10.5	13.4
4-F-2-L	46.5	8.5	7.8	6.1	19.3	4.5	
4-F-2-S	81.4	25.3	54.1	1.0	30.6	12.7	
4-F-2-TS		29.4	65.5	-0.3	33.4	14.7	5.9
4-F-3-L	46.1	7.1	8.7	6.0	18.5	4.7	
4-F-3-S	81.2	22.9	57.0	1.1	30.5	13.3	
4-F-3-TS		26.8	68.9	-0.1	33.5	15.4	5.0
4-G-1-L	47.5	13.3	8.6	3.7	20.9	4.8	
4-G-1-S	75.2	19.3	53.2	1.0	29.6	12.7	
4-G-1-TS		21.9	72.3	-0.2	33.4	16.1	5.7
4-G-2-L	47.3	10.5	8.9	3.8	19.7	5.2	
4-G-2-S	78.2	17.8	59.3	0.7	29.6	14.2	
4-G-2-TS		20.2	76.3	-0.3	32.9	17.2	4.3
4-G-3-L	46.7	8.0	9.2	3.75	18.8	5.2	
4-G-3-S	78.4	20.4	58.5	0.65	29.8	13.9	
4-G-3-TS		24.4	74.4	-0.3	33.3	16.6	3.1
4-H-1-L	47.7	14.4	7.9	4.7	21.2	3.4	
4-H-1-S	74.2	25.3	36.4	1.35	29.1	8.6	
4-H-1-TS		30.4	49.6	-0.2	32.8	11.0	16.8
4-H-2-L	46.4	11.6	8.7	4.7	20.1	3.7	
4-H-2-S	78.4	23.6	47.8	1.5	29.0	11.0	
4-H-2-TS		27.4	60.2	0.5	31.9	13.3	12.1
4-H-3-L	45.8	8.9	9.1	5.1	19.9	3.8	
4-H-3-S	78.2	23.2	51.1	1.05	29.3	11.7	
4-H-3-TS		27.6	64.0	-0.2	32.2	14.2	9.4

DESCRIPTION OF EXPERIMENT 5

Two liquors (A and C) were used in a study of the solubilities of Na_2CO_3 and Na_2SO_4 at liquor solids contents of 40, 45, 50, 55, and 60% at 100°C. The vessels were loaded as follows:

A-1	A-2	A-3	A-4	A-5
2500 g Liq. A	2900 g Liq. A	3200 g Liq. A	3620 g Liq. A	3940 g Liq. A
800 g H_2O	400 g H_2O	100 g H_2O	evap. 220 cc H_2O	evap. 540 cc H_2O
150 g Na_2CO_3	125 g Na_2CO_3	100 g Na_2CO_3	75 g Na_2CO_3	75 g Na_2CO_3
150 g Na_2SO_4	125 g Na_2SO_4	100 g Na_2SO_4	75 g Na_2SO_4	75 g Na_2SO_4

C-1	C-2	C-3	C-4	C-5
2600 g Liq. C	2950 g Liq. C	3250 g Liq. C	3700 g Liq. C	4030 g Liq. C
700 g H_2O	350 g H_2O	50 g H_2O	evap. 300 cc H_2O	evap. 630 cc H_2O
150 g Na_2CO_3	125 g Na_2CO_3	100 g Na_2CO_3	75 g Na_2CO_3	75 g Na_2CO_3
150 g Na_2SO_4	125 g Na_2SO_4	100 g Na_2SO_4	75 g Na_2SO_4	75 g Na_2SO_4

The systems were equilibrated at 100°C for 24 hours and then sampled in the usual manner.

BASIC SOLUBILITY DATA FROM EXPERIMENT 5

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
5-A-1-L	43.4	16.6	11.9	3.8	21.5	4.2	
5-A-1-S	45.9	16.7	16.4	3.8	22.8	5.2	
5-A-1-TS		17.5	58.9	3.8	34.6	14.8	10.9
5-A-2-L	47.1	13.4	7.5	4.5	21.1	3.5	
5-A-2-S	79.3	28.9	49.2	0.25	29.2	11.3	
5-A-2-TS		33.6	61.9	-1.0	31.7	13.7	8.4
5-A-3-L	50.2	12.0	5.3	4.9	20.1	3.1	
5-A-3-S	78.5	25.7	44.9	0.8	27.9	10.3	
5-A-3-TS		30.9	60.0	-0.8	30.9	13.1	12.2
5-A-4-L	55.2	10.1	3.6	5.2	18.9	2.8	
5-A-4-S	76.3	23.1	36.1	1.6	26.9	8.6	
5-A-4-TS		31.2	56.3	-0.6	31.9	12.2	13.5
5-A-5-L	59.2	8.0	2.6	5.35	18.7	2.6	
5-A-5-S	73.2	20.1	24.9	3.1	25.1	6.7	
5-A-5-TS		33.9	50.3	0.6	32.4	11.4	13.9
5-C-1-L	42.8	14.1	11.6	4.6	21.3	5.7	
5-C-1-S	75.9	25.3	52.1	1.15	30.1	12.5	
5-C-1-TS		28.8	64.6	0.1	32.8	14.6	7.1
5-C-2-L	45.5	12.3	8.1	4.8	21.2	5.3	
5-C-2-S	81.6	28.7	52.3	0.8	31.4	12.5	
5-C-2-TS		32.5	62.5	-0.1	33.7	14.1	5.7
5-C-3-L	49.6	10.0	5.6	5.2	19.6	5.1	
5-C-3-S	79.8	30.4	44.9	1.1	32.0	11.2	
5-C-3-TS		37.1	57.8	-0.25	36.1	13.2	3.6
5-C-4-L	53.4	8.2	4.6	5.4	18.9	4.9	
5-C-4-S	79.1	30.8	38.3	1.5	30.6	9.8	
5-C-4-TS		40.6	52.9	-0.2	35.7	11.9	5.8
5-C-5-L	59.6	5.1	--	6.0	--	--	
5-C-5-S	78.0	27.8	31.0	2.3	28.4	8.4	
5-C-5-TS		43.9	51	-0.3	--	--	--

DESCRIPTION OF EXPERIMENT 6

Sodium chloride was added to five different black liquors as a total solids content of 55%. Two levels of salt addition were used in each case. The NaCl was added as 25% aqueous solution, and the carrier water was subsequently evaporated off. The vessels were loaded as follows:

C	D	E	F	G
3690 g Liq. C 500 g NaCl soln.	3880 g Liq. D 500 g NaCl soln.	3990 g Liq. E 500 g NaCl soln.	3950 g Liq. F 500 g NaCl soln.	4040 g Liq. G 500 g NaCl soln.

The following amounts of H_2O were evaporated from each:

665 cc	855 cc	965 cc	925 cc	1015 cc

The systems were then equilibrated at 100°C and a solution sample only taken. After this sample was taken, another 500 g of NaCl solution was added to each vessel and 375 cc of H_2O evaporated from each. The system was then equilibrated for an additional 24 hours at 100°C and solution and solid samples taken in the usual manner.

BASIC SOLUBILITY DATA FROM EXPERIMENT 6

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	NaCl	Total Na	Total S	Organic
6-C-1-L	55.5	8.9	3.0	5.05	6.4	20.4	4.3	
6-C-2-L	56.4	6.8	2.0	4.8	12.4	22.3	4.0	
6-C-2-S	75.2	26.0	19.1	2.25	14.7	30.3	5.9	
6-C-2-TS		40.3	31.8	0.3	16.3	36.3	7.2	9.2
6-D-1-L	56.7	8.4	2.4	4.95	7.2	19.8	2.4	
6-D-2-L	56.8	6.8	1.9	4.6	12.5	20.4	2.0	
6-D-2-S	75.8	37.9	14.0	2.2	8.0	30.1	4.0	
6-D-2-TS		60.5	22.8	0.4	4.7	37.2	5.3	9.8
6-E-1-L	58.2	7.9	2.6	5.55	6.8	20.6	3.4	
6-E-2-L	57.5	4.7	1.4	5.3	12.6	20.8	3.1	
6-E-2-S	77.7	29.4	13.0	2.1	23.2	31.6	3.6	
6-E-2-TS		45.0	20.3	0.2	29.9	38.4	3.9	5.3
6-F-1-L	56.7	7.4	2.8	5.4	6.6	20.5	3.4	
6-F-2-L	57.0	6.4	3.4	5.0	12.1	21.1	3.2	
6-F-2-S	76.8	11.5	10.6	1.9	38.9	31.4	3.5	
6-F-2-TS		14.9	15.5	-0.2	56.7	38.2	3.6	8.3
6-G-1-L	57.7	7.1	3.6	3.8	6.5	20.2	3.7	
6-G-2-L	57.9	5.7	2.6	3.6	12.2	21.6	3.6	
6-G-2-S	68.7	21.5	12.3	2.1	9.8	27.2	4.6	
6-G-2-TS		48.1	28.6	-0.3	5.9	36.6	6.4	13.5

DESCRIPTION OF EXPERIMENT 7

Sodium thiosulfate was added to several different black liquors at a total solids content of about 55%. The thiosulfate was added as a 25% by weight aqueous solution and the water was subsequently evaporated off. The experiment was carried out at 100°C. The vessels were loaded as follows:

E-1	G-1	H-1	C-1	C-2
3990 g Liq. E	4040 g Liq. G	4240 g Liq. H	3690 g Liq. C	3690 g Liq. C
900 g $Na_2S_2O_3$ soln.	900 g $Na_2S_2O_3$ soln.	900 g $Na_2S_2O_3$ soln.	900 g $Na_2S_2O_3$ soln.	900 g $Na_2S_2O_3$ soln.
{ concentrate by using a N_2 purge			}	[see note below]
1265 cc	1315 cc	1515 cc	965 cc	965 cc

In C-2, an oxygen purge was used to carry out the concentration step. It was attempted to bubble O_2 through the liquor but that could not be done successfully.

After the vessels were prepared, the systems were equilibrated for 24 hours at 100°C and then sampled in the usual manner.

BASIC SOLUBILITY DATA FROM EXPERIMENT 7

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	$Na_2S_2O_3$	Total Na	Total S	Organic
7-E-1-L	58.8	7.6	2.4	5.2	12.8	19.0	7.4	
7-E-1-S	60.1	8.8	3.5	4.9	13.2	20.3	7.3	
7-E-1-TS		31.0	23.2	0.1	20.4	44.3	5.7	21.6
7-G-1-L	59.1	6.8	3.1	3.45	16.5	19.0	8.0	
7-G-1-S	62.1	9.1	4.2	2.9	16.0	20.3	7.7	
7-G-1-TS		26.4	12.2	-1.3	12.2	30.1	5.5	42.6
7-H-1-L	58.8	9.2	2.5	2.7	13.8	18.6	6.5	
7-H-1-S	72.1	22.5	9.1	1.8	7.7	27.5	5.2	
7-H-1-TS		38.9	17.2	0.8	0.1	38.7	3.5	27.8
7-C-1-L	56.9	9.2	3.7	4.5	16.4	20.0	8.6	
7-C-1-S	70.0	21.2	19.7	2.9	10.2	25.8	9.1	
7-C-1-TS		36.9	40.5	0.7	2.1	33.4	9.7	17.0
7-C-2-L	57.2	9.3	3.6	4.3	17.1	20.2	8.6	
7-C-2-S	69.5	20.5	19.6	2.9	10.8	25.9	9.0	
7-C-2-TS		36.3	42.3	0.9	1.9	33.9	9.6	16.3

DESCRIPTION OF EXPERIMENT 8

In this experiment, the solubilities of Na_2CO_3 and Na_2SO_4 in five different liquors were examined at a temperature of 120°C. The Na_2CO_3 and Na_2SO_4 were added as a 20% by weight aqueous solution containing equal parts of carbonate and sulfate. The vessels were loaded as follows:

A	C	D	E	H
2980 g Liq. A 1250 g soln. evap. 580 cc H_2O	3030 g Liq. C 1250 g soln. evap. 630 cc H_2O	3200 g Liq. D 1250 g soln. evap. 800 cc H_2O	3275 g Liq. E 1250 g soln. evap. 875 cc H_2O	3510 g Liq. H 1250 g soln. evap. 1110 cc H_2O

Note: 1250 g soln. contains 125 g of Na_2CO_3 and 125 g of Na_2SO_4. The evaporation was carried out at 100°C.

After the vessels were prepared, the contents were equilibrated at 120°C for 24 hours and then sampled in the usual manner. The pressurized sampling technique was used.

BASIC SOLUBILITY DATA FROM EXPERIMENT 8

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
8-A-1-L	48.5	10.9	6.6	4.75	19.3	3.3	
8-A-1-S	91.6	25.0	43.8	0.5	25.8	10.1	
8-A-1-TS		26.3	47.3	0.1	26.4	10.7	26.6
8-C-1-L	47.8	11.9	6.0	4.7	20.3	4.9	
8-C-1-S	80.0	29.7	50.3	1.1	31.0	12.0	
8-C-1-TS		34.5	63.4	0.0	34.2	14.0	3.9
8-D-1-L	47.5	13.0	8.1	4.5	20.3	3.6	
8-D-1-S	73.3	29.6	41.6	1.4	29.8	10.0	
8-D-1-TS		37.8	58.1	-0.2	34.5	13.2	4.7
8-E-1-L	47.1	10.5	4.9	5.3	19.7	4.0	
8-E-1-S	78.2	28.7	49.8	1.3	31.1	11.8	
8-E-1-TS		34.7	64.7	0.0	34.8	14.4	2.1
8-H-1-L	48.4	12.2	7.7	4.7	20.7	3.4	
8-H-1-S	71.3	25.3	35.6	1.4	28.0	8.5	
8-H-1-TS		33.4	52.6	-0.6	32.4	11.6	13.9

DESCRIPTION OF EXPERIMENT 9

In this experiment, the solubility data obtained in Experiment 8 was extended to 140°C. The same five liquors which were used in Experiment 8 were used in this experiment. The Na_2CO_3 and Na_2SO_4 were added as a 20% by weight aqueous solution containing equal parts of carbonate and sulfate. The vessels were loaded in the following manner:

A	C	D	E	H
2980 g Liq. A 1250 g soln. evap. 580 cc H_2O	3030 g Liq. C 1250 g soln. evap. 630 cc H_2O	3200 g Liq. D 1250 g soln. evap. 800 cc H_2O	3275 g Liq. E 1250 g soln. evap. 875 cc H_2O	3510 g Liq. H 1250 g soln. evap. 1110 cc H_2O

The evaporation of the water was carried out at 100°C in the usual manner.

After the vessels were prepared, the oil bath was brought up to 140°C and the system equilibrated for 24 hours. Solution samples were taken using the pressurized sampling technique. The vessels were then removed from the oil bath, cooled somewhat to eliminate the excess pressure, opened and a solid phase sample taken in the usual manner. Samples of the original liquors added to the vessels were also taken.

BASIC SOLUBILITY DATA FROM EXPERIMENT 9

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
9-A-1-0	50.7	8.3	2.7	5.7	17.9	2.5	
9-A-1-L	43.5	14.4	6.7	4.9	21.6	3.5	
9-A-1-S	77.1	28.4	38.7	1.0	31.6	10.7	
9-A-1-TS		32.5	48.2	-0.2	34.6	12.8	11.2
9-C-1-0	49.5	11.8	5.9	5.8	19.5	4.9	
9-C-1-L	42.1	16.4	5.8	5.0	23.3	5.1	
9-C-1-S	74.6	33.8	48.8	1.4	33.2	11.8	
9-C-1-TS		39.5	63.0	0.2	36.5	14.0	-1.3
9-D-1-0	47.8	11.0	3.6	5.3	18.3	2.7	
9-D-1-L	42.0	16.8	6.9	22.5	22.5	3.4	
9-D-1-S	71.2	35.7	44.6	32.4	32.4	10.5	
9-C-1-TS		43.6	60.3	36.5	36.5	13.5	-1.6
9-E-1-0	46.3	8.2	3.2	6.6	18.9	3.7	
9-E-1-L	41.8	13.4	4.4	5.6	21.8	4.0	
9-E-1-S	69.8	30.9	44.5	1.5	31.7	11.0	
9-E-1-TS		38.8	62.6	-0.3	36.2	14.2	-0.5
9-H-1-0	43.9	9.3	2.7	5.7	19.0	2.6	
9-H-1-L	42.4	15.4	6.6	5.0	22.3	3.4	
9-H-1-S	69.1	34.5	40.8	1.5	33.2	9.7	
9-H-1-TS		43.9	57.5	-0.2	38.5	12.8	-1.9

DESCRIPTION OF EXPERIMENT 10

This experiment was designed to examine the solubility of $CaCO_3$ in black liquors. Solid $CaCO_3$ was added to black liquors at 55% solids and the experiment carried out at 100°C. The reaction vessels were prepared as follows:

C-1,2	D-1,2	E-1,2	F-1,2	G-1,2
3690 g Liq. C	3880 g Liq. D	3950 g Liq. E	3990 g Liq. F	4040 g Liq. G
40 g $CaCO_3$	40 g $CaCO_3$	40 g $CaCO_3$	40 g $CaCO_3$	40 g $CaCO_3$
evap. 290 cc H_2O	evap. 480 cc H_2O	evap. 550 cc H_2O	evap. 590 cc H_2O	evap. 640 cc H_2O

When the desired concentrations were reached, the system was equilibrated for 24 hours at 100°C and a solution sample (Sample 1) was taken. Then an additional 24-hour equilibration period was allowed and a second solution sample (Sample 2) and a solid sample were taken.

A second batch of samples was prepared as follows:

A-3	B-3	H-3	I-3	G-3
3620 g Liq. A	3620 g Liq. B	4240 g Liq. H	3750 g Liq. I	3400 g Liq. G
40 g $CaCO_3$	40 g $CaCO_3$	40 g $CaCO_3$	40 g $CaCO_3$	40 g $CaCO_3$
evap. 220 cc H_2O	evap. 220 cc H_2O	evap. 840 cc H_2O	evap. 350 cc H_2O	no evap.

After the desired concentrations were reached, the systems were equilibrated at 100°C for 48 hours and sampled in the usual way.

BASIC SOLUBILITY DATA FROM EXPERIMENT 10

Sample	Total Solids	Total Calcium	$CaCO_3$
10-C-1-L	52.9	0.0088	0.022
10-C-2-L	53.3	0.0194	0.0484
10-C-2-S	74.0	11.4	28.4
10-C-2-TS		18.9	47.3
10-D-1-L	54.3	0.0197	0.0492
10-D-2-L	54.5	0.0203	0.0507
10-D-2-S	64.9	12.4	30.9
10-D-2-TS		35.0	87.6
10-E-1-L	54.3	0.0235	0.0588
10-E-2-L	54.6	0.0341	0.0851
10-E-2-S	68.2	18.6	46.4
10-E-2-TS		42.2	105.5
10-F-1-L	54.2	0.0043	0.0108
10-F-2-L	54.6	0.0043	0.0108
10-F-2-S	70.3	14.8	36.9
10-F-2-TS		30.0	75.0
10-G-1-L	54.4	0.0168	0.0420
10-G-2-L	54.5	0.0182	0.0455
10-G-2-S	68.1	17.9	44.8
10-G-2-TS		40.8	102.0
10-A-3-L	52.9	0.0245	0.0613
10-A-3-S	70.0	9.0	22.4
10-A-3-TS		17.3	43.2
10-B-3-L	55.7	0.0104	0.0260
10-B-3-S	58.4	2.1	5.2
10-B-3-TS		19.7	49.3
10-H-3-L	54.6	0.0328	0.082
10-H-3-S	68.3	6.7	16.7
10-H-3-TS		15.1	37.8
10-I-3-L	51.6	0.0333	0.0833
10-I-3-S	69.9	17.8	44.6
10-I-3-TS		32.9	82.3
10-G-3-L	45.0	0.0174	0.0435
10-G-3-S	64.2	19.8	49.6
10-G-3-TS		36.5	91.2

DESCRIPTION OF EXPERIMENT 11

Analyses were performed on evaporator scale obtained from one of the mills and on two liquor samples (with and without NSSC liquor added) from the same evaporator. The scale specimen showed evidence of layering and so samples were taken of the inner layer and the outer layer of the scale. A composite scale sample was also taken by crushing a relatively large piece. The results of the analyses were as follows:

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
Liquor with NSSC added	16.1	11.1	4.5	5.1	18.5	2.9	66.1
Liquor with no NSSC	17.0	11.3	5.7	4.9	18.8	3.0	65.2
Composite scale	88.6	32.6	37.6	0.4	28.8	8.6	26.9
Outer scale	92.7	37.6	38.9	0.0	28.6	8.8	23.7
Inner scale	90.7	38.6	33.5	-0.6	29.4	7.8	26.0

Note: The solid scale samples were dissolved in H_2O and diluted up to 200 ml. The total solids for the scales were back calculated based on the measured solids of the diluted samples.

DESCRIPTION OF EXPERIMENT 12

A test was carried out to determine what liquor substances were likely to precipitate under severe conditions. Five different liquors were concentrated to between 65 and 70% solids and held for 24 hours at 120°C. Solution and solid phase samples were taken in the usual manner as were samples of original liquor. The vessels were prepared as follows:

B	D	F	G	I
4440 g Liq. B evap. 1040 cc H_2O	4820 g Liq. D evap. 1420 cc H_2O	4860 g Liq. F evap. 1460 cc H_2O	4980 g Liq. G evap. 1580 cc H_2O	4800 g Liq. I evap. 1400 cc H_2O

After the desired degree of concentration was reached, the liquors were equilibrated at 120°C for 24 hours and then sampled as usual.

BASIC SOLUBILITY DATA FROM EXPERIMENT 12

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
12-B-1-0	51.0	9.6	2.5	8.8	19.6	3.6	
12-B-1-L	64.9	3.6	2.0	8.2	17.7	3.0	
12-B-1-S	78.7	20.9	21.6	2.8	22.6	6.4	
12-B-1-TS		38.2	41.2	-2.6	27.5	9.8	23.5
12-D-1-0	47.6	10.8	3.8	5.3	18.6	2.7	
12-D-1-L	65.5	6.3	2.1	3.7	16.3	2.4	
12-D-1-S	72.6	19.9	5.5	4.0	20.3	2.9	
12-D-1-TS		54.2	14.1	5.0	30.4	4.2	24.8
12-F-1-0	46.7	7.8	4.7	6.3	18.5	4.0	
12-F-1-L	65.6	4.6	2.8	5.8	16.7	3.4	
12-F-1-S	75.5	21.2	10.6	3.7	22.6	4.6	
12-F-1-TS		48.1	23.2	0.3	32.2	6.5	22.5
12-G-1-0	45.6	7.9	3.6	4.5	18.7	4.3	
12-G-1-L	63.9	3.1	2.5	4.5	18.8	4.0	
12-G-1-S	79.4	34.1	13.0	2.6	26.7	4.8	
12-G-1-TS		60.3	21.9	1.0	33.4	5.5	16.1
12-I-1-0	47.4	7.0	6.0	4.8	17.4	4.2	
12-I-1-L	64.7	3.6	2.3	5.2	16.2	3.4	
12-I-1-S	80.1	42.7	7.7	4.5	28.8	3.3	
12-I-1-TS		75.3	12.2	3.9	39.3	3.2	6.9

DESCRIPTION OF EXPERIMENT 13

Five different liquors to which a 50% NaOH solution had been added were concentrated to 60% solids, equilibrated for 24 hours at 100°C and sampled in the usual manner. The vessels were prepared as follows:

A	C	D	G	H
3950 g Liq. A	4040 g Liq. C	4190 g Liq. D	4330 g Liq. G	4560 g Liq. H
139 cc 50% NaOH	134 cc 50% NaOH	154 cc 50% NaOH	140 cc 50% NaOH	200 cc 50% NaOH
evap. 650 cc H_2O	evap. 735 cc H_2O	evap. 895 cc H_2O	evap. 1045 cc H_2O	evap. 1255 cc H_2O

After the desired concentration was reached the liquors were equilibrated at 100°C for 24 hours and then sampled in the usual manner. A sample of original liquor was also taken.

BASIC SOLUBILITY DATA FROM EXPERIMENT 13

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
13-A-1-0	51.3	6.6	2.6	5.9	17.0	2.6	
13-A-1-L	59.1	7.3	2.1	8.6	19.9	2.5	
13-A-1-S	70.8	23.0	7.5	5.2	23.5	2.9	
13-A-1-TS		46.2	15.4	0.2	28.8	3.5	34.4
13-C-1-0	49.1	13.7	5.8	5.6	19.7	4.7	
13-C-1-L	54.8	7.9	2.7	8.7	20.3	4.2	
13-C-1-S	75.9	33.0	20.8	4.0	29.7	6.2	
13-C-1-TS		48.6	32.1	1.1	35.6	7.5	14.1
13-D-1-0	47.8	11.7	3.7	5.2	18.1	2.7	
13-D-1-L	57.7	7.2	1.7	8.9	18.9	2.4	
13-D-1-S	72.4	33.0	11.4	5.1	26.8	3.6	
13-D-1-TS		60.9	21.9	1.0	35.3	5.2	14.4
13-G-1-0	45.2	12.2	3.7	3.1	18.3	4.1	
13-G-1-L	57.6	5.6	2.7	7.9	19.5	3.8	
13-G-1-S	72.7	28.7	14.5	4.55	27.4	5.1	
13-G-1-TS		52.7	26.8	1.1	35.6	6.5	15.0
13-H-1-0	44.0	9.4	3.0	5.5	19.1	2.6	
13-H-1-L	58.4	7.1	1.7	10.1	20.0	2.3	
13-H-1-S	66.0	17.2	5.5	8.2	23.3	2.6	
13-H-1-TS		43.4	15.4	3.2	31.8	3.4	31.6

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DESCRIPTION OF EXPERIMENT 14

Part I

This experiment was run to study the effect of pH on the solubility of the organics in the liquor and to look at the reversibility of precipitation phenomena caused by pH change. Five different liquors were treated with HCl and the solubilities determined. Sufficient NaOH to neutralize the HCl was then added and the solubilities redetermined.

Five vessels were prepared as follows:

14-B	14-C	14-E	14-F	14-I
3290 g Liq. B	3440 g Liq. C	3680 g Liq. E	3600 g Liq. F	3580 g Liq. I
390 cc 37% HCl	265 cc 37% HCl	300 cc 37% HCl	280 cc 37% HCl	240 cc 37% HCl
evap. 180 cc H_2O	evap. 240 cc H_2O	evap. 500 cc H_2O	evap. 410 cc H_2O	evap. 360 cc H_2O

The acid was slowly added to the liquors before they were put in the vessels in order to prevent boil over. A small amount of additional water was used to transfer the acidified liquors into the vessels. This was subsequently evaporated off before the equilibration period. The treated liquors were equilibrated for 24 hours at 100°C and solution Sample 1 taken. Liquor I was an exception. At the end of the concentration period, the shear pin coupling the stirrer to the drive gave way. A solution sample was then taken. The vessel was then pulled from the oil bath and disassembled. Hard solids on the bottom were broken free. From 50 to 100 ml of liquor was lost in doing this. The necessary NaOH was then added to the liquor, the vessel closed and put back in the hot bath.

After the solution sample from the acidified liquors was taken, concentrated (50%) NaOH solution was added to each vessel and the water content of the NaOH solution evaporated off. The amounts added and evaporated were as follows:

14-B	14-C	14-E	14-F	14-I
250 cc 50% NaOH	170 cc 50% NaOH	190 cc 50% NaOH	175 cc 50% NaOH	150 cc 50% NaOH
190 cc H_2O	130 cc H_2O	145 cc H_2O	135 cc H_2O	115 cc H_2O

The liquors were then equilibrated at 100°C for 12 hours and a solution sample taken in the usual manner. This was Sample 2. A solid sample was also taken.

Part II

An attempt was made to observe the effect of lowering the pH of a liquor by measuring the changes in liquor viscosity. Liquor E was used for this test. The liquor was heated up to about 75-77°C on a hot plate and the viscosity measured with a Brookfield viscometer. The experiment was carried out on 830 g of Liquor E. Initially 1.0N HCl was added to the liquor. This was changed to 4N HCl in the latter part of the experiment. The liquor was stirred after each addition of acid to homogenize the liquor before the viscosity was measured.

BASIC SOLUBILITY DATA FROM EXPERIMENT 14

Part I

Sample	Total Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na	Total S	Organic
14-B-0	51.1	9.5	2.0	8.9	18.6	3.5	
14-B-1-L	44.9	10.4	2.4	0.8	21.3	3.2	
14-B-2-L	52.0	7.3	1.7	8.4	21.0	2.4	
14-B-2-S	61.9	15.0	6.1	.75	24.5	2.8	
14-B-2-TS		30.4	29.6	3.3	31.4	3.6	35.0
14-C-0	48.7	14.3	6.2	5.8	20.3	4.7	
14-C-1-L	43.5	17.0	6.8	0.5	24.9	5.2	
14-C-2-L	49.8	12.0	4.0	6.05	22.2	3.9	
14-C-2-S	73.1	27.5	30.1	2.8	28.6	8.1	
14-C-2-TS		36.4	45.1	0.9	32.3	10.5	15.2
14-E-0	46.6	8.6	2.9	6.2	17.7	3.4	
14-E-1-L	43.7	9.8	3.4	0.2	21.8	3.8	
14-E-2-L	52.0	7.0	2.3	6.15	20.5	2.8	
14-E-2-S	53.1	7.0	2.8	6.15	20.4	2.9	
14-E-2-TS	No significant solid phase in sample						
14-F-0	46.9	8.0	4.5	6.3	18.05	3.8	
14-F-1-L	43.0	9.5	6.6	0.3	22.5	4.6	
14-F-2-L	51.5	6.4	4.6	6.2	20.2	3.3	
14-F-2-S	52.8	6.6	4.1	6.0	19.8	3.3	
14-F-2-TS	No significant solid phase in sample						
14-I-0	47.5	7.0	6.3	4.8	16.95	4.0	
14-I-1-L	42.2	7.2	8.3	0.1	21.7	4.7	
14-I-2-L	50.8	5.6	5.6	5.1	19.0	3.2	
14-I-2-S	53.7	6.6	7.5	4.8	19.9	3.7	
14-I-2-TS		14.8	22.9	2.4	27.5	7.8	42.7

SUMMARY OF EXPERIMENTAL DATA FROM EXPERIMENT 14

Part II

Start with 830 g Liquor E

Cumulative 1.0N HCl Added, ml	Temperature, °C	Viscosity, cp
0.0	80	18.0
1.0	77	19.6
2.0	77	19.7
3.0	75	21.7
4.0	75	21.5
5.0	75	20.9
10.0	75	24.4
15.0	76	20.1
20.0	76	Not measured

From this point on the experiment was continued with 4N HCl

Cumulative 4N HCl Added, ml	Temperature, °C	Viscosity, cp
15	78	19.8
20	77	18.2
25	77	19.1
30	77	19.0
35	77	20.6
40	78	19.5

DESCRIPTION OF EXPERIMENT 15

Solubilities of Na_2CO_3 and Na_2SO_4 were determined in a high solids sucrose solution, a high lignin liquor, and a low lignin liquor at 100°C. The low and high lignin liquors were prepared from Liquor I. Starting with 30 lb of Liquor I, 950 cc of concentrated HCl (37%) was added slowly while stirring. The solid phase sludge which precipitated was then separated from the remainder of the liquor. Five hundred cc of 50% NaOH waS then added to the solids to redissolve them. This was the lignin rich liquor. One hundred fifty cc of 50% NaOH were added to the original liquor which remained in solution. This was the lignin poor liquor.

Three vessels were prepared as follows:

15-1	15-2	15-3
2720 g cane sugar	about 3 liters of the	about 3 liters of the
680 g H_2O	high lignin liquor	low lignin liquor
175 g Na_2CO_3	150 g Na_2CO_3	150 g Na_2CO_3
175 g Na_2SO_4	150 g Na_2SO_4	150 g Na_2SO_4

The vessels were equilibrated at 100°C for 24 hours and a solution sample taken in the usual manner.

SOLUBILITY DATA FROM EXPERIMENT 15

Sample	Solids	Na_2CO_3	Na_2SO_4	Na_2O	Total Na
15-1-L	81.2[a]	3.6	3.5	0.2	--
15-2-L	49.0	5.4	4.8	16.8	33.1
15-3-L	44.5	13.1	8.6	5.2	24.1

[a]Calculated from inputs, not measured.

APPENDIX III

MATERIAL BALANCES ON SOLUBILITY EXPERIMENTS

Material balances were constructed for each of the carbonate-sulfate solubility runs. These balances consist of a comparison of the known inputs to the stirred vessels with the amounts of materials found in the solution and the solid phases (the outputs). Conservation of the total amount of solids is assumed for all of the runs. One additional conservation relationship is required to determine the absolute amount of solid phase present. Initial attempts at material balances used water as the tie element. The total water input was used to determine the amount of solution phase (all water was assumed to be in the solution phase), and the amount of solid phase was calculated from the total solids balance. These attempts were not very successful, because small errors in the wa er input could cause large errors in the amount of solid phase calculated. It was not possible to control the wa er input to the degree of accuracy required.

The balances presented in the following tables are all based on conservation of the sum of Na_2CO_3 and Na_2SO_4 over the solubility run. Since Na_2CO_3 and Na_2SO_4 are the major components of the solid phase in these experiments, it is logical to use them as the tie elements for determining the amount of solid phase.

The amount of solid phase is calculated from

$$S = T \frac{(Q_i - Q_L)}{(Q_s - Q_L)} \qquad (3)$$

where

S = weight of solid phase, g

T = total solids in system, g

Q_i = Na_2CO_3+Na_2SO_4 in input solids, % on solids

Q_L = Na_2CO_3+Na_2SO_4 in solution phase, % on solids

Q_S = Na_2CO_3+Na_2SO_4 in solid phase, % on solids

Attempts to use other measurements (such as Na_2O or total sodium) as the bases for material balances were generally less successful, because they were too sensitive to small inaccuracies in the data. All quantities in the subsequent tables are expressed in grams. The amounts of input liquors were not measured in Experiment 3. The material balances for this experiment are arbitrarily based on 2000 g of liquor solids.

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 3

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
3-A-1: Input	2000	--	150	34	104	326	52
Solution	1837	1050	70	44	94	312	45
Solid	163	--	65	5	5	36	5
3-A-1: Output	2000	1050	135	49	99	348	50
3-B-1: Input	2000	--	182	32	172	364	72
Solution	1867	810	108	26	120	327	65
Solid	133	--	67	12	3	52	4
3-B-1: Output	2000	810	175	38	123	379	69
3-C-1: Input	2000	--	104	84	118	330	100
Solution	1946	1415	90	51	93	307	93
Solid	54	--	18	30	0	20	7
3-C-1: Output	2000	1415	108	81	93	327	100
3-D-1: Input	2000	--	226	52	96	350	54
Solution	1766	1050	76	30	88	284	42
Solid	234	--	131	40	2	75	10
3-D-1: Output	2000	1050	207	70	90	359	52
3-E-1: Input	2000	--	170	42	120	378	74
Solution	1844	1005	72	28	101	305	65
Solid	156	--	86	27	2	52	7
3-E-1: Output	2000	1005	158	55	103	357	72
3-F-1: Input	2000	--	158	82	124	356	80
Solution	1958	1410	153	53	90	321	69
Solid	42	--	17	18	0	15	4
3-F-1: Output	2000	1410	170	71	90	336	73
3-G-1: Input	2000	--	160	60	82	358	82
Solution	1839	1000	41	28	75	309	74
Solid	161	--	96	55	0	60	12
3-G-1: Output	2000	1000	137	83	75	369	86
3-H-1: Input	2000	--	198	48	104	358	52
Solution	2000	1410	222	34	36	288	48
Solid	0	--	0	0	0	0	0
3-H-1: Output	2000	1410	222	34	36	288	48

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 4

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
4-A-1: Input	1790	1860	240	153	80	345	68
Solution	1712	1865	202	144	82	342	65
Solid	78	--	14	33	1	18	7
4-A-1: Output	1790	1865	216	177	83	360	72
4-A-2: Input	1790	1860	190	203	80	339	79
Solution	1691	1910	156	168	85	314	70
Solid	99	--	12	58	0	23	13
4-A-2: Output	1790	1910	168	226	85	337	83
4-A-3: Input	1790	1860	155	238	80	336	87
Solution	1676	1920	139	168	85	320	70
Solid	114	--	10	78	0	29	18
4-A-3: Output	1790	1920	149	246	85	349	88
4-B-1: Input	1815	1850	267	150	135	380	84
Solution	1716	2000	221	103	136	357	70
Solid	99	--	35	57	0	35	14
4-B-1: Output	1815	2000	256	160	136	392	84
4-B-2: Input	1815	1850	217	200	135	374	95
Solution	1664	1950	173	95	140	328	70
Solid	151	--	42	107	0	51	24
4-B-2: Output	1815	1950	215	202	140	379	94
4-B-3: Input	1815	1850	182	235	135	371	103
Solution	1613	1915	111	108	133	300	71
Solid	202	--	47	151	1	70	34
4-B-3: Output	1815	1915	158	259	134	370	105
4-C-1: Input	1785	1865	205	190	91	349	105
Solution	1705	1980	176	140	92	334	92
Solid	80	--	26	53	0	29	12
4-C-1: Output	1785	1980	202	193	92	363	104
4-C-2: Input	1785	1865	155	240	91	343	116
Solution	1647	1955	120	137	91	301	92
Solid	138	--	40	98	0	47	22
4-C-2: Output	1785	1955	160	235	91	348	114
4-C-3: Input	1785	1865	120	275	91	340	124
Solution	1646	1990	94	163	91	305	100
Solid	139	--	37	101	0	44	22
4-C-3: Output	1785	1990	131	264	91	349	122

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 4 (Continued)

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
4-D-1: Input	1790	1855	299	165	74	365	70
Solution	1711	1905	255	130	82	337	41
Solid	79	--	25	54	0	25	10
4-D-1: Output	1790	1905	280	184	82	362	51
4-D-2: Input	1790	1855	249	215	74	359	81
Solution	1683	1880	210	150	78	332	64
Solid	107	--	34	69	0	34	15
4-D-2: Output	1790	1880	244	219	78	366	79
4-D-3: Input	1790	1855	214	250	74	356	89
Solution	1617	1860	150	153	82	309	63
Solid	173	--	47	113	1	56	25
4-D-3: Output	1790	1860	197	266	83	365	88
4-E-1: Input	1785	1865	255	157	92	385	85
Solution	1706	1915	217	119	94	345	73
Solid	79	--	26	50	0	29	11
4-E-2: Output	1785	1915	243	169	94	374	84
4-E-2: Input	1785	1865	205	207	92	379	96
Solution	1647	1915	166	110	93	324	72
Solid	138	--	36	99	0	46	22
4-E-2: Output	1785	1915	202	209	93	370	94
4-E-3: Input	1785	1865	170	242	92	376	104
Solution	1608	1950	119	121	92	306	74
Solid	177	--	44	128	0	61	29
4-E-3: Output	1785	1950	163	249	92	367	103
4-F-1: Input	1805	1850	248	189	97	372	90
Solution	1706	1840	222	123	80	343	72
Solid	99	--	31	61	0	33	10
4-F-1: Output	1805	1840	253	184	80	376	82
4-F-2: Input	1805	1850	198	239	97	366	101
Solution	1623	1870	138	127	99	314	73
Solid	182	--	54	119	0	61	27
4-F-2: Output	1805	1870	192	246	99	375	100
4-F-3: Input	1805	1850	163	274	97	363	109
Solution	1615	1890	115	140	97	299	76
Solid	190	--	51	131	0	64	29
4-F-3: Output	1805	1890	166	271	97	363	105

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 4 (Continued)

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
4-G-1: Input	1815	1835	250	172	64	375	92
Solution	1782	1970	237	153	66	373	86
Solid	33	--	7	24	0	11	5
4-G-1: Output	1815	1970	244	177	66	384	91
4-G-2: Input	1815	1835	200	222	64	369	103
Solution	1724	1920	181	153	66	340	90
Solid	91	--	18	69	0	30	16
4-G-2: Output	1815	1920	199	222	66	370	106
4-G-3: Input	1815	1835	165	257	64	366	111
Solution	1681	1920	135	155	63	316	88
Solid	134	--	33	100	0	45	22
4-G-3: Output	1815	1920	168	255	63	361	110
4-H-1: Input	1800	1850	278	162	81	372	68
Solution	1734	1900	250	137	82	368	59
Solid	66	--	20	33	0	22	7
4-H-1: Output	1800	1900	270	170	82	390	66
4-H-2: Input	1800	1850	228	212	81	366	79
Solution	1690	1950	196	147	80	340	63
Solid	110	--	30	66	1	35	15
4-H-2: Output	1800	1950	226	213	81	375	78
4-H-3: Input	1800	1850	193	247	81	363	87
Solution	1642	1940	146	150	84	327	62
Solid	158	--	44	101	0	51	22
4-H-3: Output	1800	1940	190	251	84	378	84

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 5

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
5-A-1: Input	1595	2005	247	172	67	325	68
Solution	1595	2075	265	190	61	343	67
Solid	0	--	0	0	0	0	0
5-A-1: Output	1595	2075	265	190	61	343	67
5-A-2: Input	1750	1800	237	151	78	340	66
Solution	1721	1930	231	129	78	363	60
Solid	29	--	10	18	0	9	4
5-A-2: Output	1750	1930	241	147	78	372	64
5-A-3: Input	1855	1645	224	128	86	346	66
Solution	1813	1800	218	96	89	365	56
Solid	42	--	13	25	0	13	6
5-A-3: Output	1855	1800	231	121	89	378	62
5-A-4: Input	2025	1525	216	107	97	363	66
Solution	1964	1595	198	71	102	371	55
Solid	61	--	19	34	0	19	7
5-A-4: Output	2025	1595	217	105	102	390	62
5-A-5: Input	2190	1360	228	110	106	390	70
Solution	2046	1410	164	53	110	383	53
Solid	144	--	49	72	1	47	16
5-A-5: Output	2190	1410	213	125	111	430	69
5-C-1: Input	1620	1980	234	205	74	332	100
Solution	1588	2120	224	184	73	338	91
Solid	32	--	9	21	0	10	5
5-C-1: Output	1620	2120	233	205	73	348	96
5-C-2: Input	1745	1805	219	188	84	342	103
Solution	1677	2010	206	136	81	355	89
Solid	68	--	22	43	0	23	10
5-C-2: Output	1745	2010	228	179	81	378	99
5-C-3: Input	1850	1650	204	169	93	348	106
Solution	1744	1775	174	98	91	342	89
Solid	106	--	39	61	0	38	14
5-C-3: Output	1850	1775	213	159	91	380	103
5-C-4: Input	2030	1520	193	154	105	367	111
Solution	1922	1680	158	89	104	364	94
Solid	108	--	44	57	0	39	13
5-C-4: Output	2030	1680	202	146	104	403	107
5-C-5: Input	2195	1355	204	161	115	395	119
Solution	1958	1325	100	--	117	--	--
Solid	237	--	104	--	0	--	--
5-C-5: Output	2195	1325	204	--	117	--	--

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 6

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	NaCl	Total Sodium	Total Sulfur
6-C-1: Input	1950	1575	216	108	106	128	405	90
Solution	1835	1470	163	55	93	118	375	79
Solid	115	--	53	53	13	10	30	11
6-C-2: Input	2075	1575	216	108	106	253	454	90
Solution	1850	1430	126	37	89	230	412	74
Solid	225	--	91	72	1	37	82	16
6-C-2: Output	2075	1430	217	109	90	267	494	90
6-D-1: Input	1980	1545	204	67	98	140	388	50
Solution	1915	1460	161	46	95	138	379	46
Solid	65	--	43	21	3	2	11	4
6-D-2: Input	2105	1545	204	67	98	265	437	50
Solution	1987	1510	135	38	91	249	405	40
Solid	118	--	71	27	0	6	44	6
6-D-2: Output	2105	1510	206	65	91	255	449	46
6-E-1: Input	1970	1555	151	59	122	132	398	68
Solution	1970	1415	155	51	109	134	406	67
Solid	0	--	-4	8	13	-2	-8	1
6-E-2: Input	2095	1555	151	59	122	257	455	68
Solution	1957	1445	92	27	104	247	407	61
Solid	138	--	62	28	0	41	53	5
6-E-2: Output	2095	1445	154	55	104	288	460	66
6-F-1: Input	1995	1530	148	77	116	129	382	75
Solution	1970	1505	146	55	106	130	404	67
Solid	25	--	2	22	10	-1	-22	8
6-F-2: Input	2120	1530	148	77	116	254	453	75
Solution	2037	1535	130	69	102	246	429	65
Solid	83	--	12	13	0	47	32	3
6-F-2: Output	2120	1535	142	82	102	293	461	68
6-G-1: Input	1965	1560	146	66	83	129	393	79
Solution	1965	1440	140	71	75	128	397	73
Solid	0	--	6	-5	8	1	-4	6
6-G-2: Input	2090	1560	146	66	83	254	442	79
Solution	2033	1480	116	53	73	248	439	75
Solid	57	--	27	16	0	3	21	4
6-G-2: Output	2090	1560	143	69	73	251	460	79

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MATERIAL BALANCE SUMMARY FOR EXPERIMENT 7

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	$Na_2S_2O_3$	Total Sodium	Total Sulfur
7-C-1: Input	2050	1575	216	108	106	225+	422	181
Solution	1957	1480	180	72	88	321	391	168
Solid	93	--	34	38	1	2	31	9
7-C-1: Output	2050	1480	214	110	89	323	422	177
7-C-2: Input	2050	1575	216	108	106	225+	422	181
Solution	1959	1470	182	71	84	335	396	169
Solid	91	--	33	38	1	2	31	9
7-C-2: Output	2050	1470	215	109	85	337	427	178
7-E-1: Input	2075	1550	152	59	122	225+	416	160
Solution	2068	1450	157	50	108	265	394	153
Solid	7	--	2	2	0	1	3	0
7-E-1: Output	2075	1450	159	52	108	266	397	153
7-G-1: Input	2070	1555	146	67	83	225+	411	170
Solution	2042	1410	139	63	71	337	388	163
Solid	28	--	7	3	0	3	8	2
7-G-1: Output	2070	1410	146	66	71	340	396	165
7-H-1: Input	2085	1540	173	50	106	225+	420	139
Solution	2085	1460	192	52	56	288	388	135
Solid	0	--	0	0	0	0	0	0
7-H-1: Output	2085	1460	192	52	56	288	388	135

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 8

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
8-A-1: Input	1760	1890	250	166	86	366	66
Solution	1567	1665	171	103	74	302	52
Solid	193	--	51	91	0	51	21
8-A-1: Output	1760	1665	222	194	74	353	73
8-C-1: Input	1750	1900	302	214	87	387	101
Solution	1496	1635	178	90	70	304	73
Solid	254	--	88	161	0	87	36
8-C-1: Output	1750	1635	266	251	80	391	109
8-D-1: Input	1780	1870	293	180	81	375	69
Solution	1650	1825	215	134	74	335	59
Solid	130	--	49	76	0	45	17
8-D-1: Output	1780	1825	264	210	74	380	76
8-E-1: Input	1765	1885	249	174	100	382	84
Solution	1585	1780	166	78	84	312	63
Solid	180	--	62	116	0	63	26
8-E-1: Output	1765	1780	228	194	84	375	89
8-H-1: Input	1790	1860	268	167	88	388	68
Solution	1670	1780	204	128	79	346	57
Solid	120	--	40	63	0	39	14
8-H-1: Output	1790	1780	244	191	79	385	71

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 9

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
9-A-1: Input	1760	1890	250	166	86	366	66
Solution	1684	2190	243	113	83	364	59
Solid	76	--	25	37	0	26	10
9-A-1: Output	1760	2190	268	150	83	390	69
9-C-1: Input	1750	1900	302	214	87	387	101
Solution	1592	2190	261	93	80	371	81
Solid	158	--	62	100	0	58	22
9-C-1: Output	1750	2190	323	193	80	429	103
9-D-1: Input	1780	1870	293	180	81	375	69
Solution	1716	2370	288	118	76	386	58
Solit	64	--	28	39	0	23	9
9-D-1: Output	1780	2370	316	157	76	409	67
9-E-1: Input	1765	1885	249	174	100	382	84
Solution	1635	2280	219	72	92	357	66
Solid	130	--	51	82	0	47	18
9-E-1: Output	1765	2280	270	154	92	404	84
9-H-1: Input	1790	1860	268	167	88	388	68
Solution	1738	2360	268	115	87	388	59
Solid	52	--	23	30	0	20	7
9-H-1: Output	1790	2360	291	145	87	408	66

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 12

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
12-B-1: Input	2265	1135	217	57	199	444	82
Solution	2065	1120	74	41	170	366	62
Solid	200	--	76	82	-5	55	20
12-B-1: Output	2265	1120	150	123	165	421	82
12-D-1: Input	2290	1110	248	87	121	426	62
Solution	2053	1080	129	43	76	335	49
Solid	237	--	128	33	12	72	10
12-D-1: Output	2290	1080	257	76	88	407	59
12-F-1: Input	2270	1130	177	107	143	420	91
Solution	2088	1095	96	59	121	349	71
Solid	182	--	88	42	1	59	12
12-F-1: Output	2270	1095	184	101	122	408	83
12-G-1: Input	2270	1130	180	82	102	425	98
Solution	2094	1180	65	52	94	394	84
Solid	176	--	106	39	2	59	10
12-G-1: Output	2270	1180	171	91	96	453	94
12-I-1: Input	2280	1120	160	137	110	397	96
Solution	2082	1135	75	48	94	338	71
Solid	198	--	149	24	8	78	6
12-I-1: Output	2280	1135	224	72	102	416	77

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 13

Identity	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
13-A-1: Input	2130	1380	134	53	201	405	53
Solution	2130	1470	155	45	183	425	53
Solid	0	--	0	0	0	0	0
13-A-1: Output	2130	1470	155	45	183	425	53
13-C-1: Input	2085	1425	272	115	190	450	93
Solution	1848	1520	146	50	161	375	78
Solid	237	--	115	76	3	84	18
13-C-1: Output	2085	1520	261	126	164	459	96
13-D-1: Input	2120	1415	234	74	196	430	54
Solution	1959	1435	141	33	175	370	47
Solid	161	--	98	35	2	57	8
13-D-1: Output	2120	1435	239	68	177	427	55
13-G-1: Input	2070	1435	239	73	144	421	80
Solution	1873	1380	105	51	148	365	71
Solid	197	--	104	53	2	70	13
13-G-1: Output	2070	1380	209	104	150	435	84
13-H-1: Input	2160	1455	189	60	229	472	52
Solution	2042	1455	145	35	207	408	47
Solid	118	--	51	18	4	38	4
13-H-1: Output	2160	1455	196	53	211	446	51

Members of Group Project 3136

MATERIAL BALANCES FOR EXPERIMENT 14

Material balances were constructed for the different runs in Experiment 14. The purpose is to estimate the amounts of solid phase formed and how much of it can be accounted for by known inorganic compounds. Each run consists of two parts: first HCl was added and a solution sample only taken, then NaOH was added and a solution and solid sample taken. When HCl is added to the liquors it reacts with the Na_2O compounds. It is assumed that water is formed in this reaction as if the HCl reacted with NaOH. The balance is constructed by assuming conservation of total solids and water, and that all water appears as solution phase. Components in the solid phase in the Run 1's are calculated by the difference between the input and that found in the solution. The amount of Na_2O expected to be consumed by the HCl added is shown in parentheses. The Na_2O input for the Run 2's is found by adding the Na_2O equivalent of the NaOH put in to the Na_2O in the solution for Run 1. The amounts of solution and solid phase in the second runs are found by the combined solids and water balances. The compositions of the liquid and "true solids" are then used to complete the material balance.

MATERIAL BALANCE SUMMARY FOR EXPERIMENT 14

Sample	Total Solids	H_2O	Na_2CO_3	Na_2SO_4	Na_2O	Total Sodium	Total Sulfur
14-B-1: Input	1770	1800	160	34	150	314	59
14-B-1-L	1465	1800	153	35	12	312	47
14-B-1-TS	305	--	7	-1	(144)	2	12
14-B-2: Input	1960	1800	160	34	160	423	59
14-B-2-L	1950	1800	142	33	164	410	47
14-B-2-TS	10	--	3	3	0	3	0
14-B-2: Output	1960	1800	145	36	164	413	47
14-C-1: Input	1735	1780	240	104	97	340	79
14-C-1-L	1370	1780	233	93	7	342	71
14-C-1-TS	365	--	7	11	(99)	-2	8
14-C-2: Input	1865	1780	240	104	108	415	79
14-C-2-L	1765	1780	212	71	107	392	69
14-C-2-TS	100	--	36	45	1	32	11
14-C-2: Output	1865	1780	248	116	108	424	80
14-E-1: Input	1780	1755	148	50	106	304	58
14-E-1-L	1365	1755	134	46	3	297	52
14-E-1-TS	415	--	14	4	(111)	7	6
14-E-2: Input	1925	1755	148	50	115	387	58
14-E-2-L	1900	1755	133	44	117	390	53
14-E-2-TS	25	--	0	0	0	0	0
14-E-2: Output	1925	1755	133	44	117	390	53
14-F-1: Input	1750	1770	135	76	106	305	64
14-F-1-L	1335	1770	127	88	4	301	62
14-F-1-TS	415	--	8	-8	(104)	4	2
14-F-2: Input	1885	1770	135	76	109	383	64
14-F-1-L	1880	1770	120	87	116	380	62
14-F-1-TS	5	--	0	0	0	0	0
14-F-2: Output	1885	1770	120	87	116	380	62
14-I-1: Input	1755	1840	119	107	82	289	68
14-I-1-L	1345	1840	97	111	1	292	63
14-I-1-TS	410	--	22	-4	(89)	-3	5
14-I-2: Input	1870	1840	119	107	90	358	68
14-I-2-L	1900	1840	106	106	97	361	61
14-I-2-TS	-30		-4	-7	-1	-8	-2
14-I-2: Output	1870	1840	102	99	96	353	59